공학박사학위논문

Methods to Improve Properties of Polyurethane Foam Using Liquid-Type Additives

액상첨가제를 활용한 폴리우레탄 폼의 특성 향상 방안

2017년 2월

서울대학교 대학원

화학생물공학부

이 영 범

Abstract

Methods to Improve Properties of Polyurethane Foam Using Liquid-Type Additives

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Polyurethane is a polymer material made by the exothermic reaction between polyol and isocyante. It has many good properties that it has been widely used in various kinds of industry. [1] Especially rigid polyurethane foam is one of best thermal insulation materials and it has been used as a main insulator for cryogenic industries such as Liquefied Natural Gas (LNG) storage tanks, LNG carriers etc. [1-4]

Blowing agent is a material which makes polyurethane cellular material and gives polyurethane foam insulating ability. CFCs were typical blowing agents. But they have not been used because they destroy the stratospheric ozone layer. HCFC-141b was chosen for an alternative to CFCs. However, although small ozone depletion

potential (ODP) of HCFC-141b compared to CFCs, additional alternative blowing agents with zero ODP such as hydroflurocarbons (HFCs) have been needed because of tougher environmental regulations since 2000s.

LNG demand has risen by an estimated 7.5% per year since 2000. [5] Nowadays the price of natural gas has become higher and the efficiency of propulsion systems of liquefied natural gas (LNG) carriers has improved. Due to these trends, required boil-off rate (BOR) has been lowered from 0.15%/day to 0.12%/day for conventional LNG carriers with sizes between 125,000 m^3 and 170,000 m^3. This requirement of BOR can be satisfied by using a rigid polyurethane foam (PUF) blown by 1,1-dichloro-1-fluoroethane (HCFC-141b) as an insulator but we cannot use it anymore. So new alternative blowing agent should be used instead of HCFC-141b. But the use of alternative blowing agent can make another problem like deterioration of thermal conductivity due to its relatively high thermal conductivity. [1, 3, 6-12]

This research introduces HFCs as an alternative to HCFC-141b and discuss characteristics of rigid PUFs prepared with HFCs and shows its application to LNG carriers. We also discuss effects of liquid-type additives to enhance properties of rigid PUFs under laboratory atmosphere and the possibility of their adaptability to mass production type PUFs. For these three liquid-type additives, propylene carbonate (PC), perfluoroalkane (PFA), and acetone, were introduced. The addition of perfluoroalkane induced the small cell size of the PUFs. Based on the morphology, thermal conductivity, and compressive strength, it is suggested that

the perfluoroalkane is an efficient liquid-type additive for the improving the thermal performance of PUFs. [13, 14]

Based on this result, a mass production type rigid PUF for a LNG carrier was manufactured and evaluated for BOR, mechanical strengths over operation temperature range, coefficient of thermal expansion (CTE), and thermal shock stability for LNG carriers. The calculated BOR of the manufactured rigid PUF is below 0.12%/day, which satisfies the recent and tough BOR specification for LNG carriers. Other properties also meet the specifications for a conventional LNG carrier. [13]

Consequently, it is expected that the results in this paper will bring low BOR (<0.12%/day) LNG carries with rigid PUFs using ODP free blowing agents and contribute environmental protection through saving energy and preserving the ozone layer in the stratosphere. Besides that, the product of this paper will reduce the time required to construct the raw material system and make the blending system configuration process easier.

Keywords: Polyurethane Foam, Insulator, Blowing Agent, Ozone Depletion Potential, Additive, Thermal conductivity

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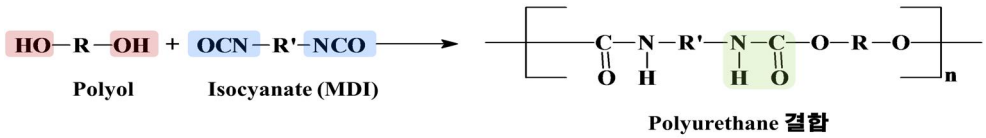
CHAPTER 1 : Introduction

1.1. Research motivation

Polyurethane is a polymer material made by the exothermic reaction between polyols and isocyantes. Polyurethane shows many good properties so it has been used in many industrial fields such as shoes, furniture and so on. Especially rigid polyurethane foam is one of the best insulating materials due to its low thermal conductivity as shown in Figure 1-2. [15-17] Blowing agent is a component that makes polyurethane have cellular structure and gives it thermal insulating capacity by existing in the closed cell as gas phase. Since 1930 when organic synthesized refrigerant, ChloroFluoroCarbons (CFCs) had appeared on the market they had been widely adopted as a refrigerant for vapor compression cycle and as a blowing agent for insulating material. But since Mario Molina and Sherwood Rowland etc. proved that CFCs depletes the ozone layer in the stratosphere in the 1970's, the use and the production of CFCs had been banned. In addition to that the alternative to CFCs, HCFC-141b also had been limited after 2000 in the developed countries, although its Ozone Depleting Potential (ODP) is about one to eleventh (1/11) of CFC-11. So many research projects have been doing about new alternatives, HFCs. [18]

LNG industry fields such as LNG storage tank, LNG pipe, LNG carriers etc., use polyurethane foam in various parts as a main insulator. [19-30] Nowadays the price of natural gas has become higher and the efficiency of propulsion systems of liquefied natural gas (LNG) carriers has improved. Due to these trends, required

boil-off rate (BOR) has been lowered from 0.15%/day to 0.12%/day for conventional LNG carriers with sizes between 125,000 m^3 and 170,000 m^3. This requirement of BOR can be satisfied by using a rigid polyurethane foam (PUF) blown by 1,1-dichloro-1-fluoroethane (HCFC-141b) as an insulator. HCFC-141b has been used for an alternative to CFCs. But we cannot use it anymore because of tougher environment regulation. Although small ozone depletion potential (ODP) of HCFC-141b compared to CFCs, it still depletes the stratospheric ozone layer and additional alternative blowing agents with zero ODP such as hydroflurocarbons (HFCs) have been needed since 2000s. [18] But the use of alternative blowing agent can make another problem like deterioration of thermal conductivity due to its relatively high thermal conductivity. This research introduces use of HFCs and additives to enhance properties of rigid PUFs under laboratory atmosphere and also under a mass production environment.



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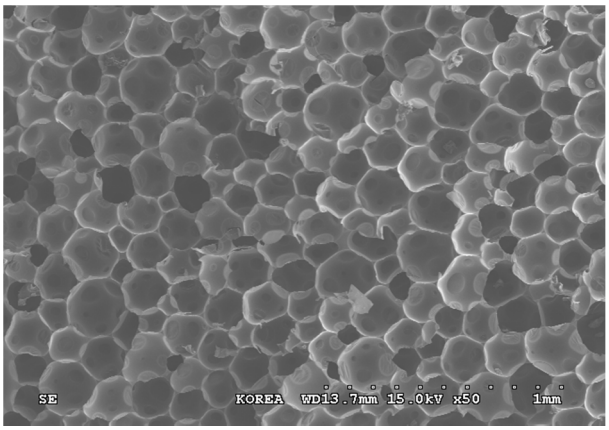


(b)

Figure 1-1 Basic knowledge; (a) basic synthesis reaction of polyurethane, (b) scanning electron microscope (SEM) of polyurethane foam [1, 3, 31]

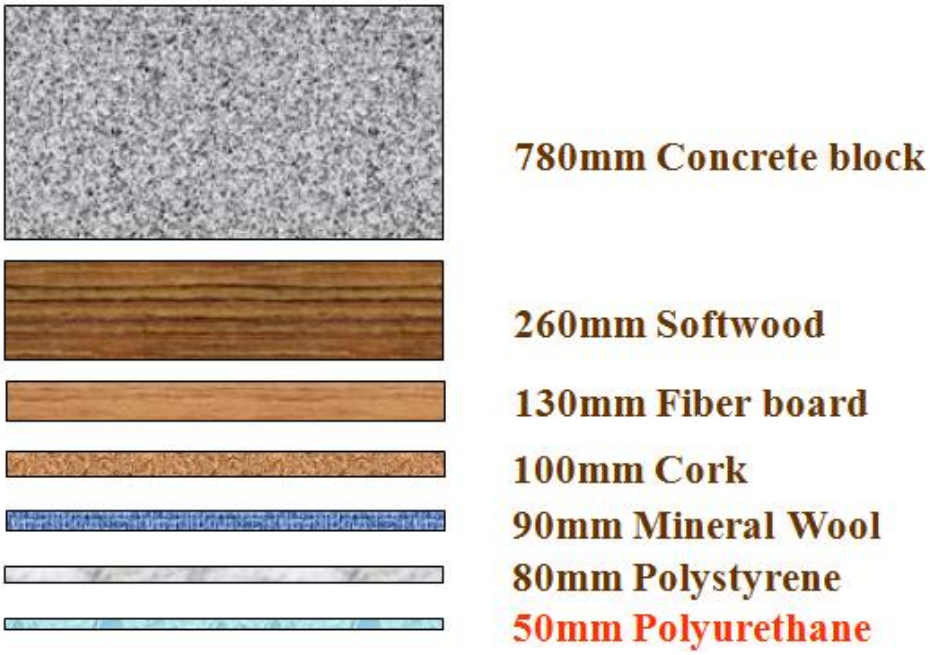
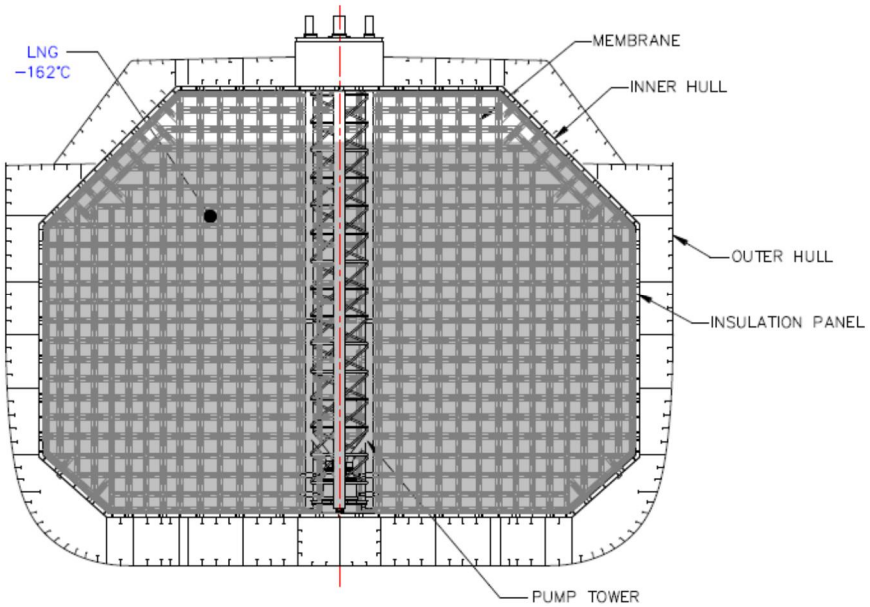


Figure 1-2. Equivalent thickness of various building material [1, 3]



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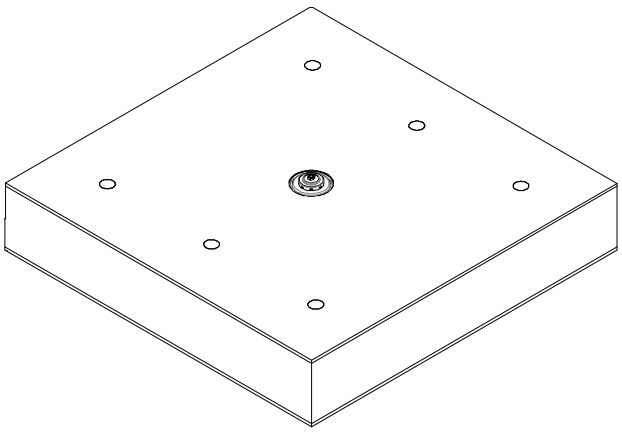


(b)

Figure 1-3. Typical structure of a LNG carrier; (a) a basic structure of a cargo containment system, (b) a basic insulation panel [2]

1.2. Trend in blowing agent selection and checking the effect of various additives on properties of polyurethane foam

Since 1930 when organic synthesized refrigerants, ChloroFluoroCarbons (CFCs) had appeared on the market they had been widely adopted as a refrigerant for vapor compression cycle and as a blowing agent for insulating material. But since Marlio Molina and Sherwood Rowland proved that CFCs deplete the ozone layer in the stratosphere in the 1970's, the use and the production of CFCs had been banned. In addition to that the alternative to CFCs, HCFC-141b also had been limited after 2000 in the developed countries, although its Ozone Depleting Potential (ODP) is about one to eleventh (1/11) of CFC-11. So many research projects have been doing about new alternatives, HFCs. [18]

The effects of liquid-type additives on the morphology, thermal conductivity, and mechanical strength of polyurethane foams (PUFs) were investigated. The PUFs synthesized with perfluoroalkane or silicone surfactant showed a smaller average cell diameter and a lower thermal conductivity than PUFs prepared with propylene carbonate or acetone. The average cell diameter of the PUFs decreased and the thermal conductivity also decreased when the perfluoroalkane content was 0.0 to 2.0 php (parts per hundred polyol by weight). The perfluoroalkane likely acted as a nucleating agent during the formation of the PUFs. The addition of perfluoroalkane induced the smaller cell size of the PUFs probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate. The

smaller cell size appears to be the main reason for the improvement in the thermal insulating and the mechanical properties of these PUFs in addition case of perfluoroalkane. The compressive strength of the PUFs prepared with perfluoroalkane was higher than the PUFs prepared with the propylene carbonate or acetone. Based on the morphology, thermal conductivity, and compressive strength, it is suggested that the perfluoroalkane is an efficient liquid-type additive for improving the insulation performance of PUFs.

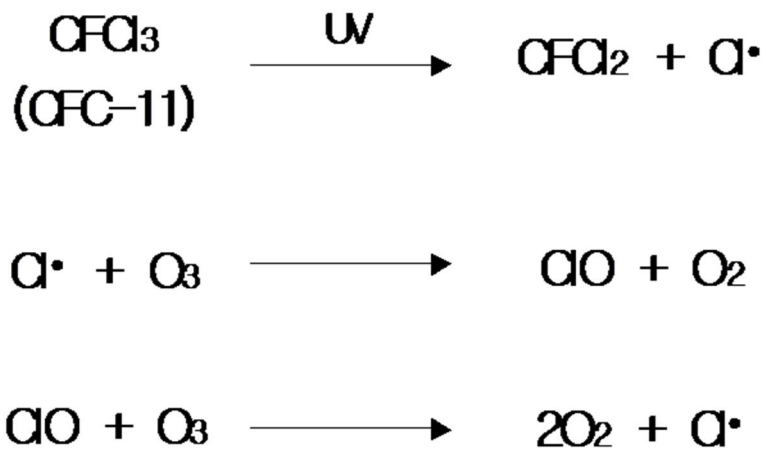


Figure 1-4. Ozone layer destruction mechanism by CFC-11 [32]

Table 1-1. Characteristics of various blowing agents [1, 3, 9, 13]

Blowing agent	CFC-11	HCFC-141b	HFC-365mfc	HFC-245fa
Chemical Formula	CCl_3F	CH_3CCl_2F	$CF_3CH_2CF_2CH_3$	$CH_3CH_2CHF_2$
Molecular Weight	137.4	116.9	148	134
Boiling Point [^oC]	23.8	32.9	40.2	15.3
Thermal conduct. @10^oC [mW/(mK)]	7.4	8.8	10.6	12.5
Ozone Depletion Potential (with CFC-11=1)	1.0	0.11	0	0
Global Warming Potential (with CO_2=1)	4,600	700	910	990
Atmospheric lifetime [years]	45	9.2	10.8	7.4

1.3. Research objectives

The objective of the thesis is to suggest systematic methodologies and guidelines to implement manufacturing polyurethane foam insulator through considering effects of various additives on polyurethane foam in views of thermal conductivity and various properties. Since intensive integration knowledge about the effect of several additives and optimum addition amount is required, this research suggests guidelines to chemical engineers for preparing effective blending system, and enables them to do their jobs effectively. Furthermore, the indication about the optimal addition amount about every additive makes the chemical engineer (system formulator) to decide effectively the final blending composition.

Consequently, it is expected that the results in this paper will bring low BOR (<0.12%/day) LNG carries with rigid PUFs using ODP free blowing agents and contribute environmental protection through saving energy and preserving the ozone layer in the stratosphere.

1.4. Outline of the thesis

The thesis is organized as follows. Chapter 1 suggests an explanation about research motivation, choosing and changing trend in blowing agent, and objectives of the research as introduction. As a starting point of the analysis on the effects of several additives, what kind of factors affects deeply properties of polyurethane through published papers and reports in Chapter 2. Several possible additives were selected and added to the system to take shape the effect of the mentioned factors. The quantitative relationship was checked to control the added amount of additives. Preliminary blending system for high density polyurethane foam, about 120 kg/m^3 for LNG carrier was formulated to meet the requirement of Boil-Off Rate of the stored LNG in the cargo containment. This preliminary blending system was adjusted reflecting the test results of the continuous production line using the system. The final blending system was decided through this kind of regulating method. High density polyurethane foam was produced using the commercial production line and it was evaluated to confirm whether it can be used as main insulator for a LNG carrier and the blending system was finally fixed.

This thesis will conclude the summary of the results which were demonstrated in making blending system for polyurethane foam insulator and the outline for future work.

CHAPTER 2 : Effect of Liquid-Type Additives on Properties of Polyurethane Foam

2.1. Introduction

Polyurethane is diversely used thanks to its outstanding performance in many industrial fields. Especially rigid polyurethane foam has been used as a main insulator for house insulator to cryogenic insulator and its application fields has become large. [1] Blowing agent make polyurethane a cellular material and gives it insulating ability. Although it was widely used as a blowing agent for polyurethane foam, the use of HCFC-141b has been phased out due to the ODP and HFCs have begun to replace it. [18] Two HFCs such as HFC-365mfc from Solvay and HFC-245fa from Honeywell were considered as alternative blowing agents for HCFC-141b. The ODP is zero for HFC-365mfc and HFC-245fa but their thermal conductivity is a bit higher than that of HCFC-141b. Table 1-1 summarizes properties of main blowing agents. When it comes to current LNG carriers, high price of LNG and the improved performance of propulsion system in LNG carriers require more challenging specification of boiling-off rate (BOR) than ever before, which requests higher thermal insulation performance. [13] Therefore, higher thermal conductivity of HFCs should be compensated by other additives and optimal synthesis approaches. For this basic evaluation of various additives effects was done. Various properties like density, thermal conductivity, dimensional stability, mechanical strength etc. are needed to be used as insulator for LNG industries and these properties have much relationship with one another. If the relationships among properties were found and understood fully, checking only a

few properties might indicate the total performance of the polyurethane foam. This kind of activity can be expected to reduce the needed time to develop a new blending system to satisfy the required performance.

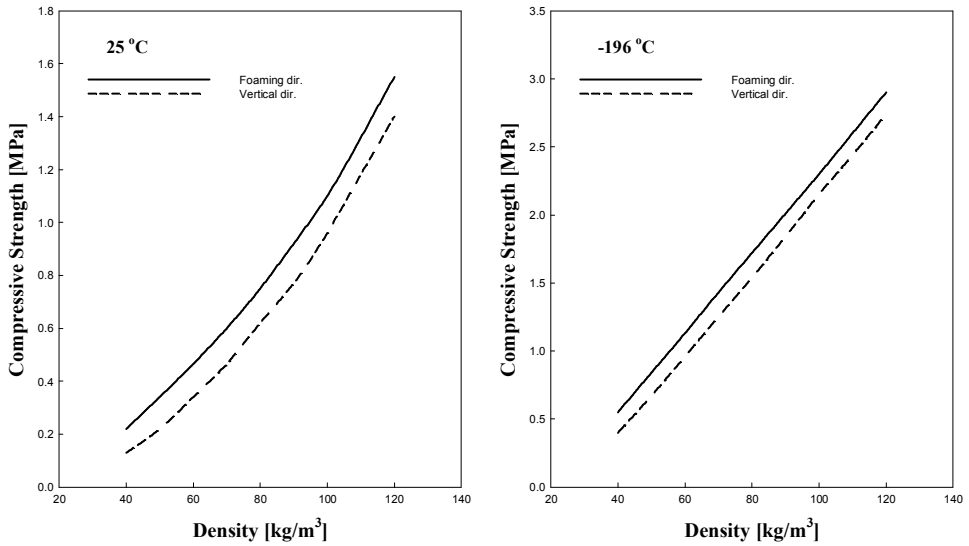
The purpose of this study is to find more efficient liquid-type additives. In this study, the effects of three different liquid-type additives (perfluoroalkane, propylene carbonate and acetone) on cell morphology, thermal insulation and mechanical properties of rigid PUFs blown by HFC-365mfc were studied using scanning electron microscope (SEM), thermal conductivity, and a universal testing machine, respectively. The addition of perfluoroalkane may induce the smaller cells size of the PUFs probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate. For the propylene carbonate and acetone, they are low viscosity liquids. The lower viscosity of the polyol mixtures is expected to form well-mixed solution and make smaller cells. These additives contributed somewhat to lowering the viscosity of the polyol and additive mixture but failed to reduce cell size of PUFs.

2.2. Factors to affect properties of polyurethane foam

One of main factors to affect properties of polyurethane foam is density. The relationships between density and compressive strength, between density and thermal conductivity are shown in Figure 2-1 to Figure 2-5. As the density increases the compressive strength of PUF also increases as shown in Figure 2-1. As the density increases the thermal conductivity of PUF also increases like Figure 2-2. So they show opposite characteristics.

Usually high mechanical strength and low thermal conductivity are needed for a LNG carrier. So we need to develop a blending system for polyurethane foam by coordinating the two conflicting characteristics which can make PUF with high mechanical strength and low thermal conductivity. From Figures 2-4 and 2-5 even the same density polyurethane foam shows low thermal conductivity and high mechanical strength if it consists of small and homogeneous cells.

Polyurethane foams with small and homogeneous cell size distribution can be obtained by using special additives and improving the reactivity. Polyurethane foam with small and homogeneous cells can be made by using proper nucleating agent or surfactants. [33] And the reactivity can be enhanced by improving the mixing effect by using low viscous components. [14] Several promising additives such as polypropylene carbonate, acetone, perfluoroalkane, were selected from these viewpoints.



(a) (b)

Figure 2-1. Typical relationship between compressive strength and density of polyurethane foam; (a) at 25 °C, (b) -196 °C [33, 34]

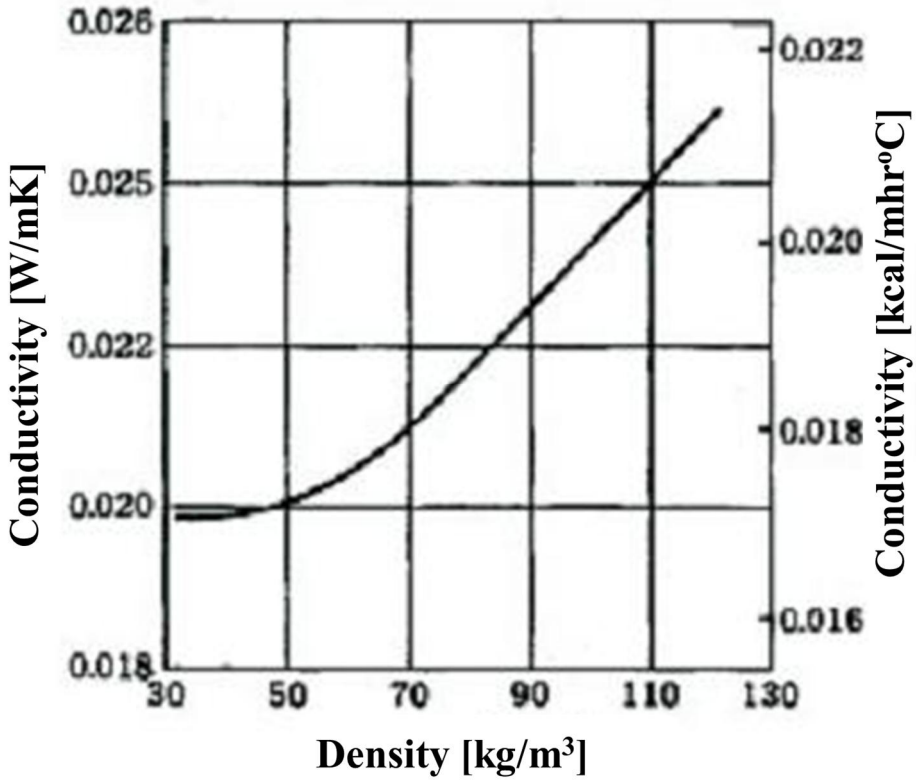


Figure 2-2. Typical relationship between thermal conductivity and density of polyurethane foams [33, 34]

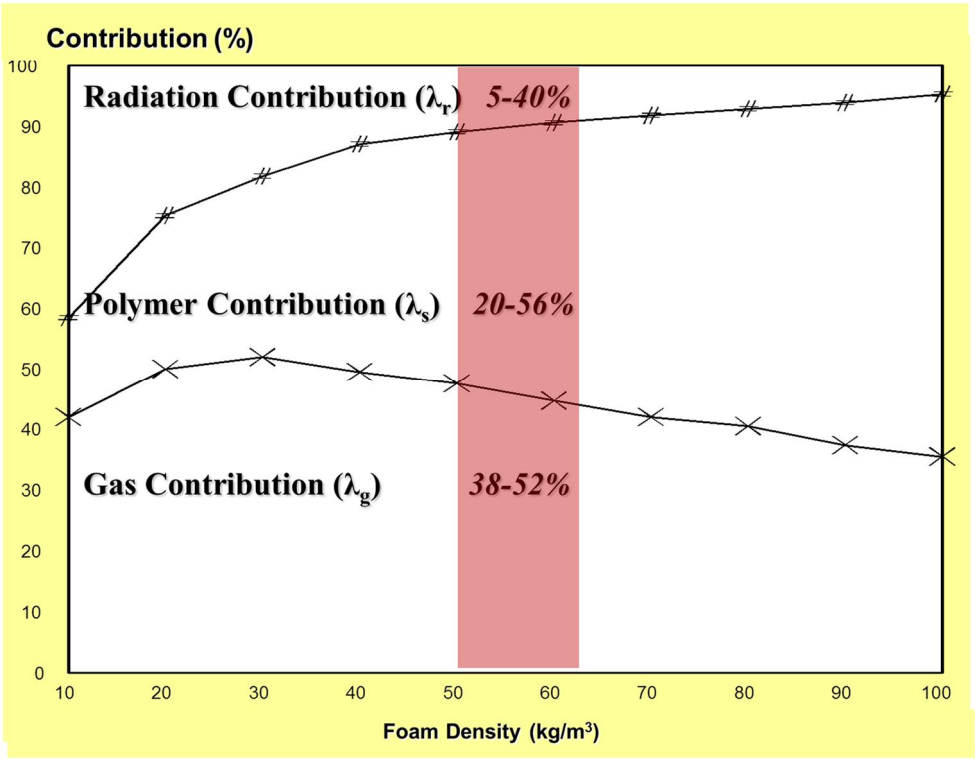


Figure 2-3. Contribution of transfer modes to heat transmission in PUF [35]

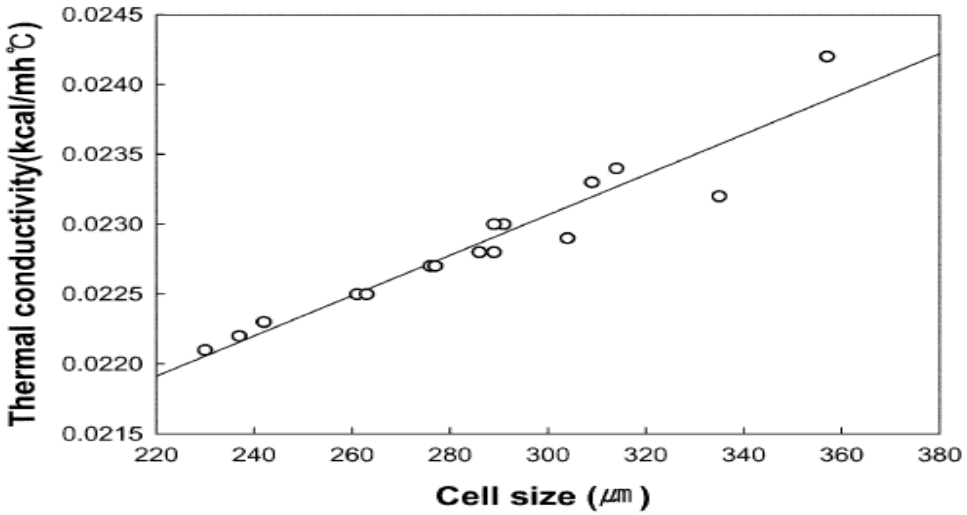


Figure 2-4. Relation between thermal conductivity and cell size of PUFs blown by distilled water only [3, 8]

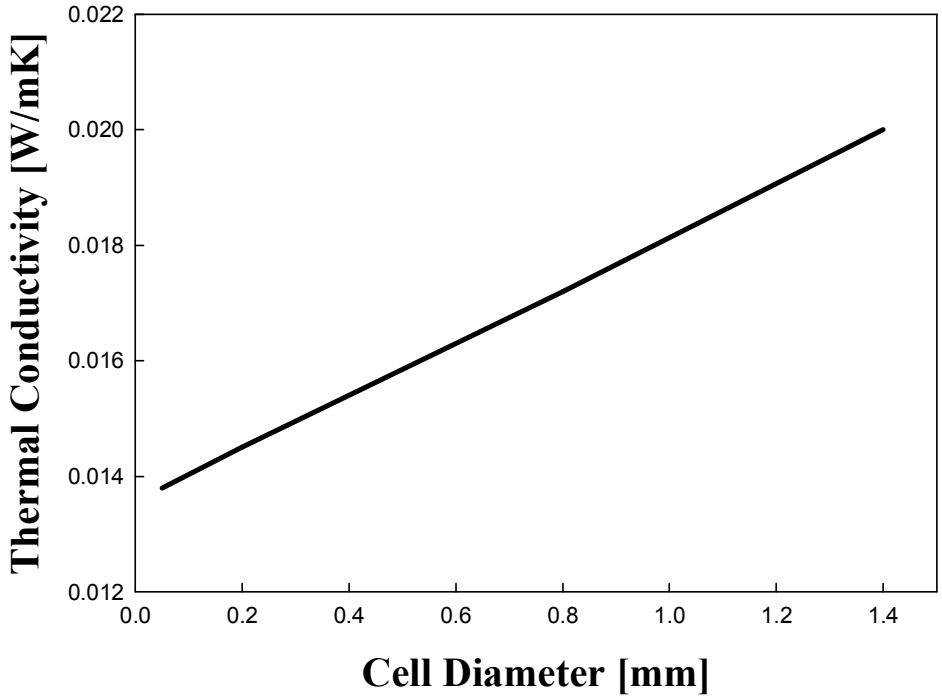


Figure 2-5. Effect of cell size on thermal conductivity of PUFs (at 0 ^{o}C) [1]

2.3. Experiment

2.3.1. Materials

The materials used in this study were obtained from commercial sources. Polymeric 4,4'-diphenylmethane diisocyanrate (MDI) was supplied by BASF Korea Ltd. (Daejeon, Korea). The average functionality of MDI was 2.9 and the NCO content was 31.2 wt %. The polyols used in this study were polyether type and polyester type polyols. Pentaerithritol (OH value5560 mg KOH/g) and sucrose-based polyether polyol (OH value5490 mg KOH/g) were supplied by BASF Korea Ltd. Glycol-based polyester polyol (OH value5300 mg KOH/g, 3200 cps) was also supplied by BASF Korea Ltd. The weight ratio of pentaerithritol-based polyether polyol, sucrose-based polyether polyol, and glycol-based polyester polyol used in this study was 30:20:50 wt %, respectively. HFC-365mfc was used as a physical blowing agent for investigating the effects of liquid-type additives. Pentamethyldiethyltriamine (PC 5) and dimethylcyclohexylamine (PC 8), which were supplied by Air Products and Chemicals, Inc. (Allentown, PA), were used as catalysts. Silicone-type surfactant (NIAX silicone L6900) was supplied from Momentive Co. (USA). The hydrophile-lipophile balance (HLB) value of the surfactant is 8.47. Three different types of liquid-type additives were used (perfluoroalkane, propylene carbonate and acetone). Perfluoroalkane (PF 5056) was supplied by 3M Co. (USA). The chemical compositions of the materials used in the preparation of the PUFs are shown in Table 2-1. The NCO index of the PUFs prepared according to Table 2-1 was 110.

Table 2-1. Chemical compositions used in the preparation of PUFs [13, 14]

Materials	Description	Weight [g]
Polyol	Polyether/polyester polyol	100.0 (50/50)
MDI	Polymeric 4,4'-diphenylmethane diisocanate	108.0
Surfactant	Silicone type (L6900)	3.0
Catalyst	Pentamethyldiethyltriamine (PC5)	0.03 ~ 0.07
	Dimethylcyclohexylamine (PC8)	0.07
Blowing agent	HFC-365mfc	9.2
	HFC-245fa	8.3
	HCFC-141b	7.3
Liquid-type additive	Perfluoroalkane	0.5~2.0
	Propylene carbonate	0.5~2.0
	Acetone	0.5~2.0

2.3.2. Preparation of polyurethane foams

Figure 2-6 shows raw materials and a process flow for production of rigid PUFs in this study. Basic processes in a laboratory scale and a mass production scale are almost same except for processed amount, and conditioning time after blending polyol mixture. In case of the mass production scale, two-day conditioning is required to stabilize polyol mixtures and to remove air bubbles generated during blending processes. In the laboratory scale, however, 150 s of a blending process to mix basic materials such as water, catalyst, polyols, blowing agent and additives are required. After that, the polymeric 4,4-diphenylmethane diisocyanate (MDI) is added to the well-prepared polyol mixture. The total solution is mixed for 60 s with a propeller-type stirrer at 7000 rpm speed. After mixing, the mixture is poured into an open mold to produce free-rise foams. Since the reaction is exothermic, the generated heat vaporizes blowing agents, which helps to make a cell structure eventually. This foamed mixture is cured at room temperature for more than five days to remove unreacted solution and to release the reaction heat.

Among raw materials, this paper investigated effects of ozone depletion potential (ODP) free blowing agents and additives on rigid PUF performance in a laboratory scale, first. Then, the investigation was reflected in optimizing conditions for a mass production scale. One of the optimum conditions for a mass production scale was prepared and characteristics of the rigid PUF manufactured in the condition are discussed in Chapter 3.

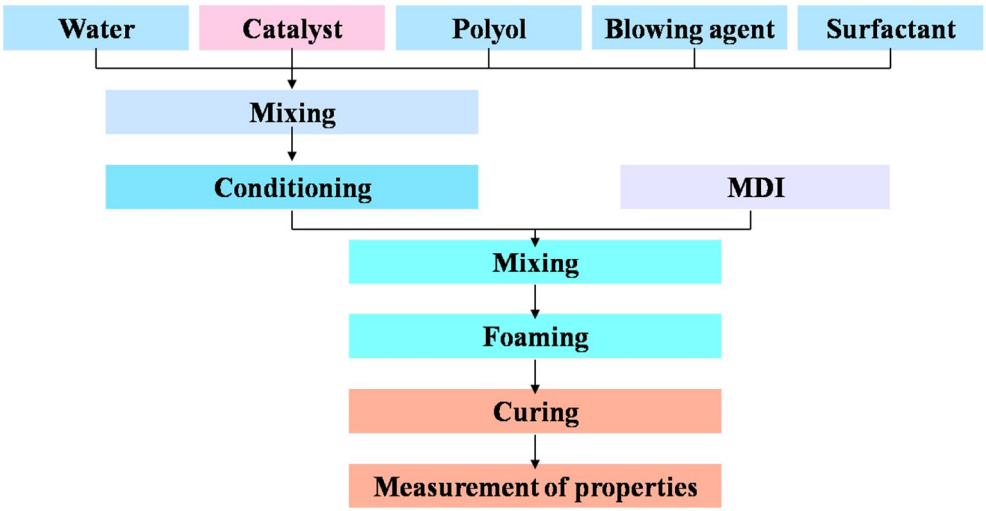


Figure 2-6. Process flow of polyurethane foam production [13]

2.3.3. Measurement and experimental conditions

Cell Morphology

The morphology of the PUFs was studied with a field emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300SE, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated with gold before scanning. The accelerating voltage was 15 kV. We counted 50 cells from the obtained SEM pictures and then the cell size was measured and averaged from the selected 50 cells.

Surface Tension Measurements

Surface tensions of the liquid-type additive (perfluoroalkane, propylene carbonate or acetone) and polyol and additive mixtures were measured using contact angle analyzer (model GonioStar 150, Surfacetech, Korea). Droplets of the solutions were dropped on the surface of glass palte. After that, contact angle between droplet and glass plate was measured. The surface tension is calculated using eq. (1): [36]

$$\cos\theta = 2\emptyset\left(\frac{\gamma_S}{\gamma_L}\right)^{\frac{1}{2}} - 1 \qquad (1)$$

where θ is the contact angle, $\emptyset$ is the ratio of molar volume of liquid and solid which is approximated to 1.0, γ_S the surface energy of solid which is glass plate (24.8 mN/m), and γ_L the surface tension of liquid.

Viscosity Measurements

Viscosity of the polyol and additive mixtures was measured using cone and plate rheometer (model AR 2000, TA Instruments). Cone angle and diameter of the fixture were 2 degree and 40 mm, respectively. Shear rate sweeps from 0.1 to 10^3 s^{-1} were performed at room temperature. The shear viscosity was obtained at the low shear rate range.

Thermal Conductivity Measurements

The thermal conductivities of PUFs were measured using a thermal conductivity analyzer (model TCA Point2, Anacon) according to the ASTM C518 standard test method. [37] The PUF sample was placed in the test section between two plates, which were maintained at different temperatures during the test. It took about 20 minutes to obtain steady state between two plates including a sample. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, the thermal conductivity of the PUFs was determined. The size of the specimen was 200 mm x 200 mm x 25 mm (width x length x thickness). The thermal conductivities of three specimens per sample were measured and averaged.

Mechanical Properties

The mechanical properties of PUF samples were measured under ambient conditions using a universal testing machine (Instron 4467). A compressive test was performed according to the ASTM D1621 test method. The size of each specimen was 50 mm x 50 mm x 50 mm (width x length x thickness), and the

speed of crosshead movement was 5.00 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test

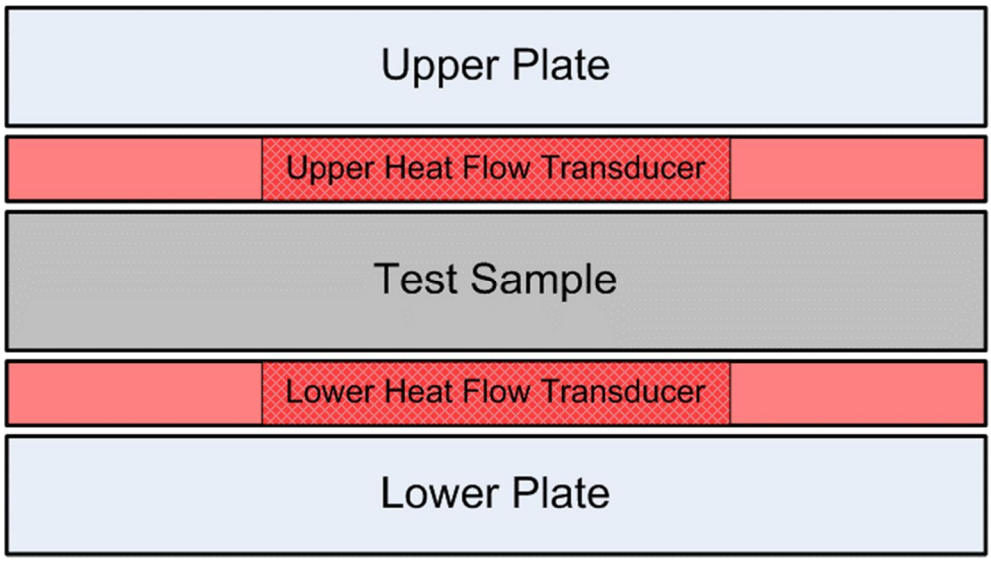


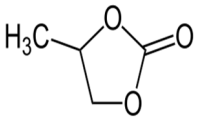
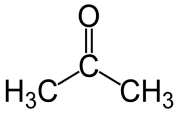
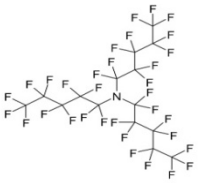
Figure 2-7. Schematic diagram for heat flow meter (HFM) method

Figure 2-8. Universal testing machine (Instron 4467)

2.4. Effects of additives on properties of polyurethane foam

As mentioned in 2.1., small size of cell structure and low density with mechanical strength are key control factors of rigid PUFs for LNG carriers. Several approaches to decreasing the size of cell structure are reported. [1, 3, 8, 10, 11] The first approach is to decrease viscosity in mixing raw materials, which could be realized by adding low viscosity additives. The second approach is to add a nucleating agent so that it can facilitate cell formation. The other approach is to add an enhancement agent to a soft PUF for thermal conductivity. In order to check the effects of these approaches, three additives were prepared as summarized in Table 2-2. Before obtaining any optimum condition for rigid PUFs, effects of each additive on rigid PUF performance were investigated.

Table 2-2. Basic properties of liquid-type additives [13, 14]

Material	Propylene carbonate	Acetone	Perfluoroalkane
Molecular formula	$C_4H_6O_3$	C_3H_8O	C_nF_{2n+2}
Melting Point [^oC]	-48.8	-95	-95 to -80
Boiling Point [^oC]	242	56	40 to 60
Density [kg/m^3]	1205	791	1780 to1800
Structural formula			

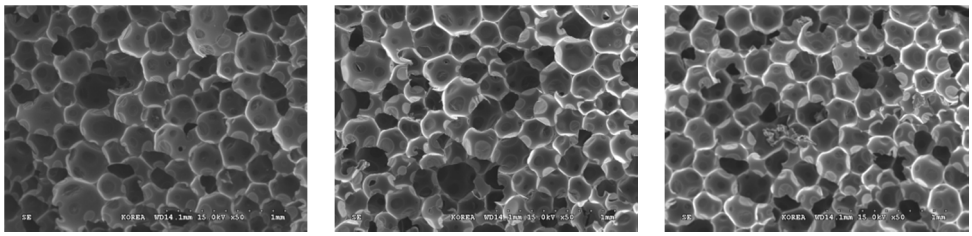
2.4.1. Blowing agent on rigid PUF performance

As mentioned in 2.1, the use of HCFC-141b has been phased out due to the ODP and HFCs have begun to replace it. Two HFCs such as HFC-365mfc from Solvay and HFC-245fa from Honeywell were considered as alternative blowing agents in this paper. The ODP is zero for HFC-365mfc and HFC-245fa but their thermal conductivity is a bit higher than that of HCFC-141b. When it comes to current LNG carrier application, high price of LNG and the improved performance of propulsion system in LNG carriers require more challenging specification of boiling-off rate (BOR) than ever before, which requests higher thermal insulation As an initial selection stage, effects of HFC-245fa or HFC-365mfc on rigid PUFs were investigated by using the same formula except their catalysts. Table 2-3 summarizes properties of rigid PUFs prepared by HCFC-141b, HFC-365mfc or HFC-245fa. They show very similar characteristics in terms of density, compressive strength and apparent thermal conductivity, but it should be noticeable that the PUF prepared by HFC-245fa with the highest thermal conductivity shows the lowest apparent thermal conductivity (23.4 mW/m K at 20 ^{o}C). This finding might indicate that the apparent thermal conductivity of foam material is dominated by various factors such as cell structures, compatibility between blowing agent and other raw materials and gas composition rather than the thermal conductivity of blowing agent itself. Further basic evaluation of various additives effects was done with HFC-365mfc instead of HFC-245fa because HFC-245fa tends to vaporize under experimental environment due to its low boiling point, 15.3 ^{o}C. Based on the further evaluation with HFC-365mfc, we optimized the chemical formula in manufacturing PUF with HFC-245fa.

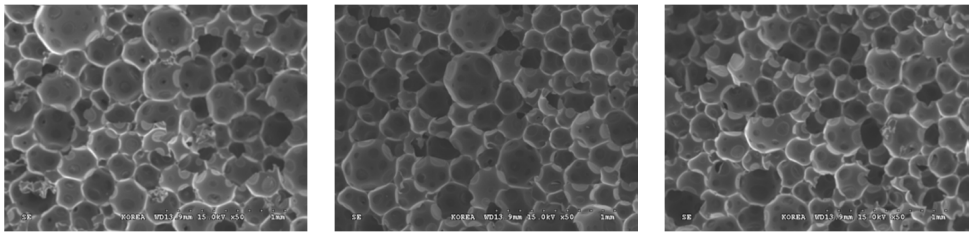
Table 2-3. Properties of rigid PUFs prepared by various blowing agents [9, 13, 14]

Property	HCFC-141b system	HFC-365mfc system	HFC-245fa system
Density [kg/m^3]	109.5	109.6	109.5
Blowing agent amount [php#]	7.3	9.2	8.3
Compressive strength [MPa]	1.13	1.13	1.11
Apparent thermal conductivity @20°C [mW/mK]	23.5	23.9	23.4

php means parts per hundred polyols by weight



(a) 294 ㎛ (top) (b) 283 ㎛ (mid.) (c) 249 ㎛ (bot.)



(d) 303 ㎛ (top) (e) 280 ㎛ (mid.) (f) 264 ㎛ (bot.)

Figure 2-9. SEM of rigid PUFs prepared by various blowing agents; (a~c) PUFs by HFC-365mfc, (d~f) PUFs by HFC-245fa [13]

2.4.2. Propylene carbonate on rigid PUF performance

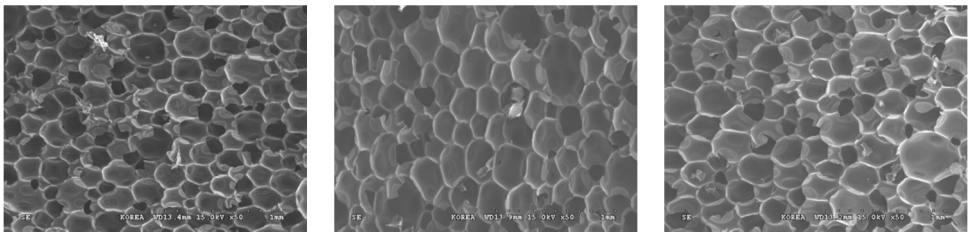
Propylene carbonate (PC) is a non-viscous liquid at ambient conditions and is expected to increase mixing efficiency in a blending system and to enhance mechanical strength. Increase of the mixing efficiency is expected due to the assumption that PC can reduce the viscosity of total solution, which might lead to uniform reaction. Enhancement of the mechanical strength is expected due to the assumption that PC can facilitate formation of hard segment in a cell structure. The effects of PC on density, compressive strength and thermal conductivity of rigid PUF are summarized in Table 2-4. Among the effects, compressive strength shows clear impact as expected but it seems to be saturated as the amount of PC increases. That is, 5% increase of compressive strength for the rigid PUF is obtained. The other effects such as density and thermal conductivity do not show any meaningful impact under the current rigid PUF formula.

Aside from these effects, phase separation issues in polyol mixtures were observed during a conditioning process. These phase separation issues should be seriously considered because mass production environment requires about two days conditioning to remove generated air during blending. As a result, it is concluded that PC is excluded in our consideration.

Table 2-4. Effects of PC on rigid PUF properties [13, 14]

PC [php*]	Density [kg/m^3]	Compressive strength [MPa]	Thermal conductivity at 24 ^{o}C [mW/mK]
0	115.2	1.16	25.9
1	114.1	1.20	26.6
2	114.5	1.22	26.2

* php means parts per hundred polyols by weight



(a) 0 php (238 μm) (b) 1 php (248 μm) (c) 2 php (246 μm)

Figure 2-10. SEM of PUFs with varying PC concentrations [13, 14]

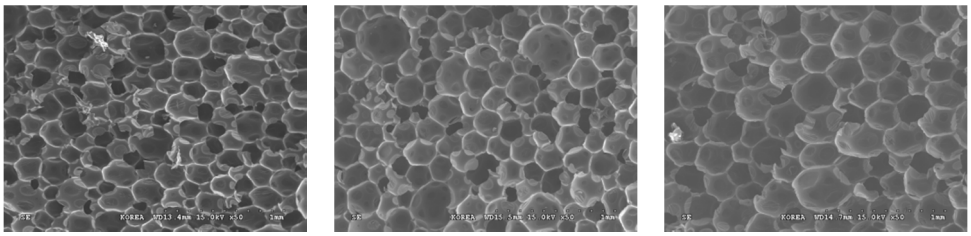
2.4.3. Effects of acetone on rigid PUF performance

Acetone is a low viscous material with high volatility and is expected to increase the mixing efficiency in a blending system. In addition, acetone is used to decrease thermal conductivity of soft polyurethane foam. The effects of acetone on density, compressive strength and thermal conductivity of rigid PUF are summarized in Table 2-5. Its effects show clearer trend than PC. That is, 15% decrease of density and 28% decrease of compressive strength are obtained as the amount of acetone increases from 0 to 2 php. On the other hand, thermal conductivity increases up to 3% as a function of acetone amount. Changes in cell structure are also large as shown in Figure 2-11. These results are speculated as follows; acetone might be vaporized during reaction, which leads to increase of gas portion within produced foam. Due to the increase of gas portion in the foam, the density of the foam decreases. In addition, the heat generated through this vaporization process accelerate growth of cell significantly. This significant cell growth helps to increase thermal conductivity but higher gas portion in the foam might deteriorate compressive strength. In this case, insulation performance and stability of structure for LNG carrier become deteriorated. Therefore, it is concluded that acetone is excluded in our consideration.

Table 2-5. Effects of acetone on rigid PUF properties [13, 14]

Acetone [php*]	Density [kg/m^3]	Compressive strength [MPa]	Thermal conductivity at 24 ^{o}C [mW/mK]
0	115.2	1.16	25.9
1	99.6	1.06	26.8
2	94.3	0.94	27.0

* php means parts per hundred polyols by weight



(a) 0 php (238 μm) (b) 1 php (251 μm) (c) 2 php (323 μm)

Figure 2-11. SEM of PUFs with varying acetone concentrations [13, 14]

2.4.4. Effects of perfluoroalkane on rigid PUF performance

Perfluoroalkane (PFA) is a mobile liquid and expected to increase the mixing efficiency in a blending system. In addition, PFA can act like surfactant to reduce surface tension of solution so that it can facilitate forming a small cell in PUF [38, 39]. The effects of PFA on density, compressive strength and thermal conductivity of rigid PUF are summarized in Table 2-6. The important point in the PFA case is that the thermal conductivity and the density of rigid PUF decreases more significantly than the compressive strength of rigid PUF as the amount of PFA increases. That is, 11% decrease of thermal conductivity, 10% decrease of density, and 5% decrease of compressive strength are obtained as a function of amount of PFA. This might come from the fact that boiling point of PFA is not high (40–60 ^{o}C) and due to its boiling point, PFA might act like a blowing agent.

It seemed to be valuable to optimize PFA effects further in varying amount of HFC-365mfc. That is, amount of blowing agent should be compensated to the extent of PFA addition to obtain the similar level of density of rigid PUF. Table 2-7 summarizes the test results. At the certain amount of blowing agent, density of rigid PUFs doesn't change meaningfully irrespective of PFA addition, but thermal conductivity and compressive strength of rigid PUFs change in the favorable direction. Specifically, at the concentration of 2 php PFA, rigid PUF has the smallest thermal conductivity (15% improvement) and the highest compressive strength (12% improvement), which comes from smaller cell size in Figure 2-10. In conclusion, addition of PFA is desirable to obtain required characteristics for rigid PUF.

Table 2-6. Effects of PFA on rigid PUF properties [13, 14]

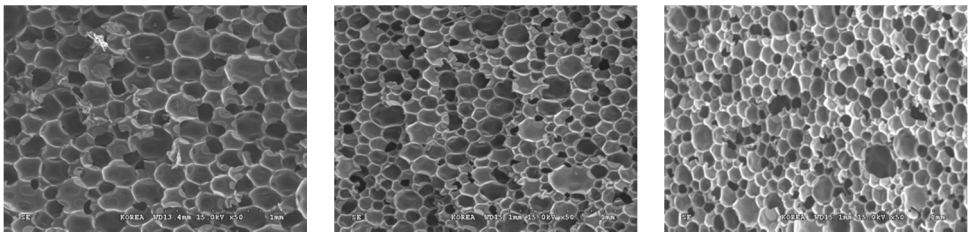
PFA [php*]	Density [kg/m^3]	Compressive strength [MPa]	Thermal conductivity at 24 ^{o}C [mW/mK]
0	115.2	1.16	25.9
1	108.1	1.20	23.2
2	103.3	1.07	23.1

* php means parts per hundred polyols by weight

Table 2-7. Effects of PFA on rigid PUF properties with decrease amount of blowing agent [13, 14]

PFA [php*]	HFC-365mfc [php*]	Density [kg/m^3]	Compressive strength [MPa]	Thermal conductivity at 24 ^{o}C [mW/mK]
0	9.2	115.2	1.16	25.9
1	9.1	114.1	1.24	23.5
2	9.0	114.5	1.28	22.8

* php means parts per hundred polyols by weight



(a) 0 php (238 μm) (b) 1 php (215 μm) (c) 2 php (155 μm)

Figure 2-12. SEM of PUFs with varying PFA and varying blowing agent concentrations [13, 14]

2.5. Conclusion

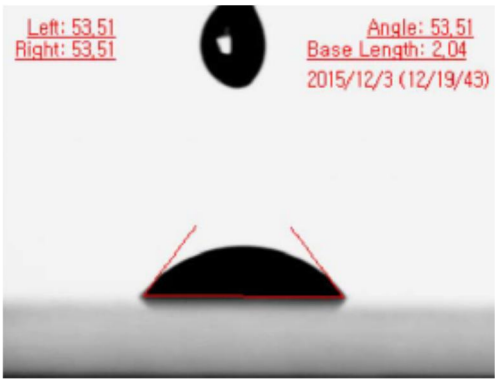
2.5.1. Surface tension of polyol solutions

In Figure 2-13, (a)–(d) shows the contact angle measurements of the polyol solution without additive (65.9 degree) and the polyol and various additive mixtures such as perfluoroalkane, propylene carbonate and acetone which are 52.2, 57.4 and 53.5 degrees when the additive content is 2.0 php. The surface tensions of additives such as perfluoroalkane, propylene carbonate and acetone were also obtained from the contact angle measurements and found to be 13.9, 40.3 and 25.1 mN/m, respectively. Table 2-8 shows the surface tensions of the polyol solution without additive (50.1 mN/m) and the polyol and various additive mixtures such as perfluoroalkane, propylene carbonate and acetone which are 21.4, 41.9 and 39.0 mN/m when the additive content is 2.0 php. From Table 2-8, the surface tension of the polyol and perfluoroalkane mixture showed the lowest value among the polyol and propylene carbonate mixture or the polyol and acetone mixture. From the results of morphology and surface tension shown in Table 2-8, it is suggested that the lower value of the surface tension has affected the polyol and perfluoroalkane mixture to create a lot of nucleation sites and it promotes the formation of dense and small cells. [14]

(a) without additive

(b) with perfluoroalkane 2.0 php#

(c) with propylene carbonate 2.0 php#



(d) with acetone 2.0 php#

Figure 2-13. Measurements of contact angle of polyol and various additive mixtures [14]

php means parts per hundred polyols by weight

Table 2-8. Cell size, density, viscosity and surface tension of polyol mixtures with additives [13, 14]

Additive	Without	Perfluoroalkane		Propylene carbonate		Acetone	
[php]	additive	1.0	2.0	1.0	2.0	1.0	2.0
Cell size [µm]	238	205	115	238	237	251	323
Density [kg/m^3]	115.2	114.1	114.5	114.1	114.5	99.6	94.3
Viscosity [Pas]	6.78	4.01	2.50	4.46	4.42	4.33	3.79
Surface tension [mN/m]	50.1	23.1	21.4	44.0	41.9	42.4	39.0

2.5.2. Cell size of PUF

The data in Figure 2-14 show average cell diameters of the PUFs with additive species and concentrations. The average cell diameters of PUFs with perfluoroalkane are smaller than those of the foams with propylene carbonate and acetone. Besides that, the cell distributions are more uniform for the foams with perfluoroalkane compared to the foams with propylene carbonate and acetone. These results are likely due to the lower surface tension of the perfluoroalkane, which allows it to be well-mixed in the polyol solutions and consequently a higher nucleation rate. [14, 40] It seems that the low-surface tension of the polyol and perfluoroalkane mixture prohibits the coalescence of bubbles and it promotes the formation of dense and small cells. Table 2-8 shows the viscosity of the polyol solutions. This result suggests that the lower value of viscosity of the polyol and the perfluoroalkane mixture has attributed to form well-mixed solution and small cell. [14] The data in Figure 2-14 suggest that propylene carbonate does not affect the cell size of the PUFs, however, it can be used as a chain extender in the preparation of PUFs. Therefore, mechanical strength of the PUFs may be increased with the addition of propylene carbonate; the result will be shown in the compressive strength section of this study. The cell size of PUFs that were prepared with acetone increased as the acetone content. Since acetone is a low viscosity liquid, it is expected to increase the mixing efficiency when it is added to the polyol mixture. The lower viscosity of the polyol and acetone mixture was expected to form well-mixed solution and smaller cells. [41, 42] However, acetone did not produce small cells size. Acetone acted more like a blowing agent and the cell wall of the foams became rather thinner. The density of PUFs with acetone is

appeared to decrease from 115.2 to 94.3 kg/m^3 when the acetone content increases from 0.0 to 2.0 php. Of course, lowering the foam density results into the increasing of foam cell sizes. As the result, the cells coalesced, lowering the compressive strength. [14]

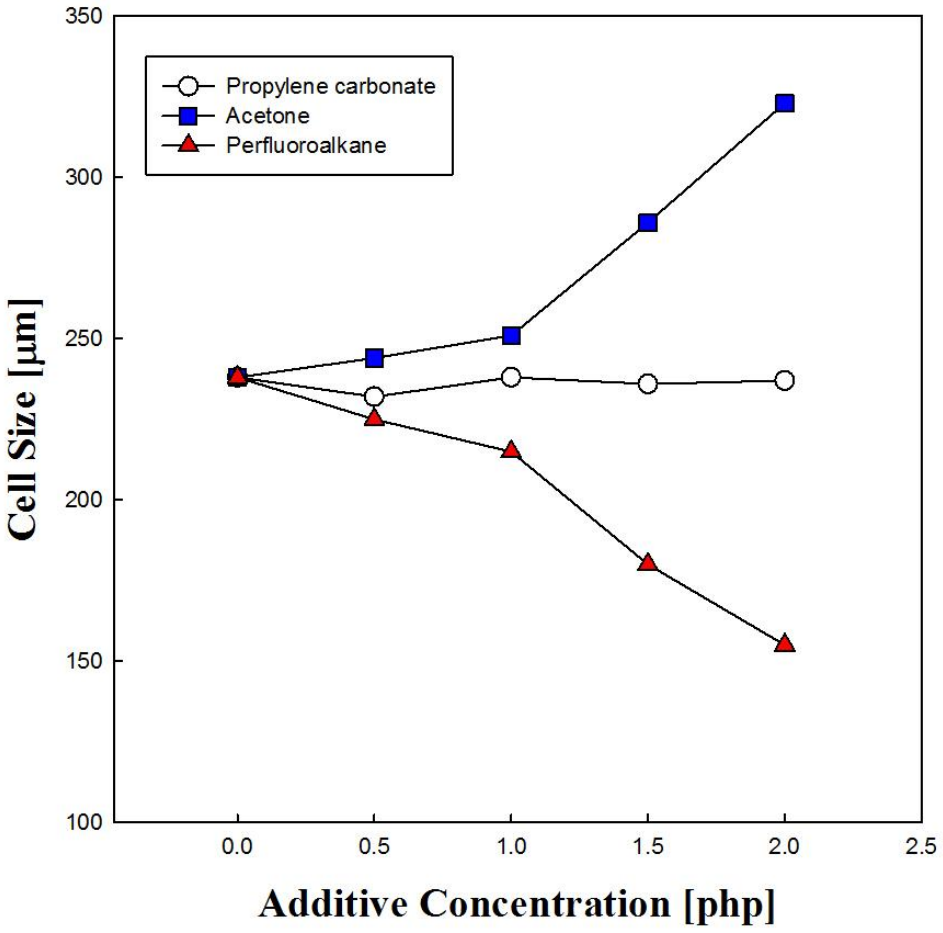


Figure 2-14. Average cell size of PUFs with various additives at different concentrations [14]

2.5.3. Thermal Conductivity of PUFs

Thermal conductivity is one of the important factors in thermal insulating materials. Effects of three different liquid-type additives on the thermal conductivity of the PUFs are shown in Figure 2-15. When the additive concentration of perfluoroalkane is increased from 0.0 to 2.0 php, the thermal conductivity of the PUFs decreased from 25.9 to 22.8 mW/mK. For the PUFs with propylene carbonate and acetone, the thermal conductivities were observed to be from 25.9 to 26.2 and from 25.9 to 27.0 mW/mK respectively with the increase of additive concentrations.

Figure 2-15 shows that PUFs with perfluoroalkane as a nucleating agent have lower thermal conductivity than neat PUFs because of their smaller average cell diameter. The PUFs with perfluoroalkane showed the lowest thermal conductivity relative to PUFs with propylene carbonate and acetone. This is probably because PUFs with perfluoroalkane provided the smallest cell size. It is thought that the perfluoroalkane creates considerable bubble nucleation during the foaming process by reducing the critical activation energy for nucleation. Figure 2-16 shows the relationship between the thermal conductivity and average cell size of the PUFs with the three different additives (perfluoroalkane, propylene carbonate and acetone). Thermal conductivity of the PUFs prepared with perfluoroalkane, propylene carbonate or acetone is decreased with a decrease of the cell size, which explains that small cell size improves the thermal insulating property. [13, 14]

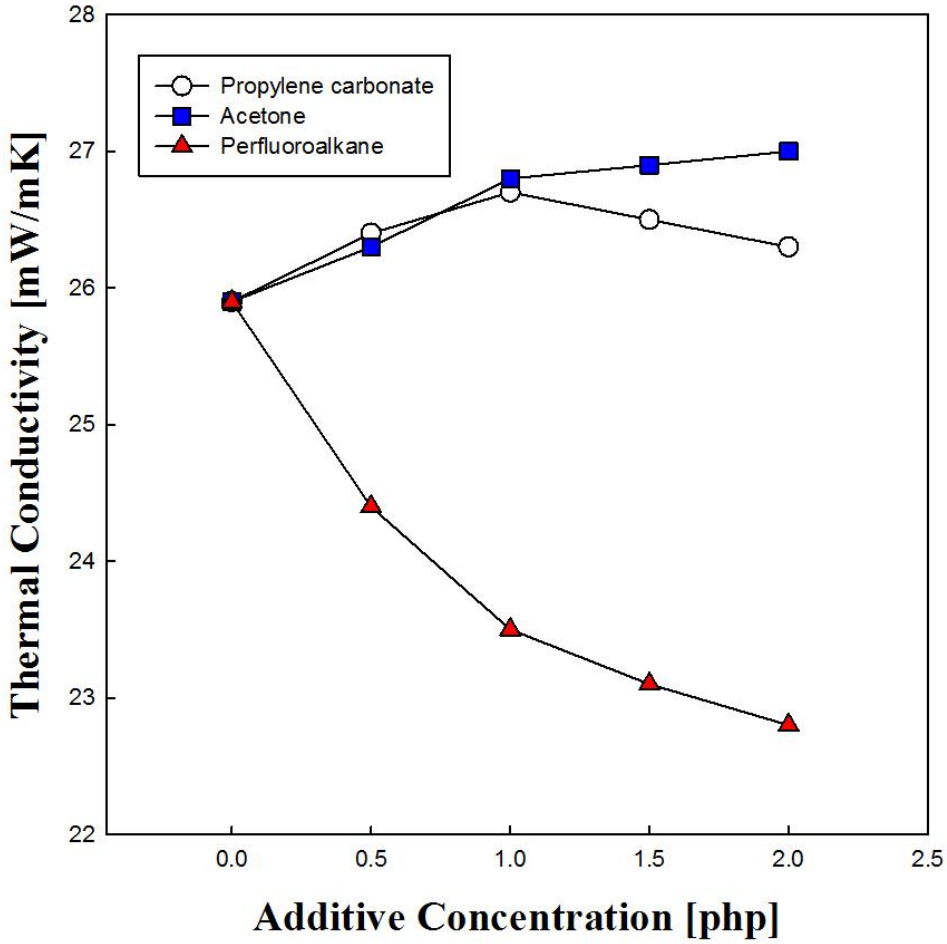


Figure 2-15. Thermal conductivity of PUFs with various additives at different concentrations [14]

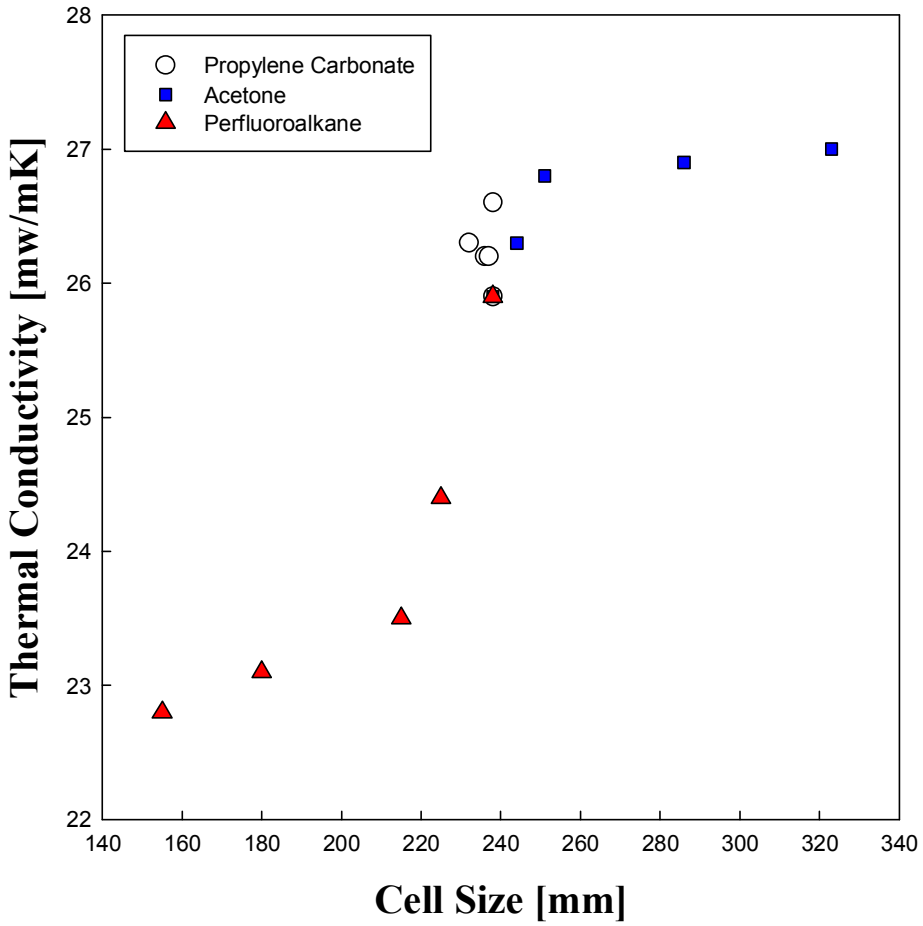


Figure 2-16. Relationship between thermal conductivity and cell size of PUFs with various additives at different concentration [14]

2.5.4. Compressive Strength of PUFs

Figure 2-17 shows the compressive strength of the PUFs prepared with the three additives at different concentrations. The compressive strength of the PUFs with perfluoroalkane and propylene carbonate increase slightly with an increase of additive contents. Average density of the PUFs prepared with perfluoroalkane and propylene carbonate was about 114 kg/m^3 (Table 2-8). The compressive strengths of the PUFs with the perfluoroalkane were found to be 1.230, 1.361, and 1.312 MPa for the additive content of 0.0, 1.0, and 2.0 php, respectively. Esmaeilnezhad et al. reported that there is a direct correlation between the microstructure and mechanical strength of the foams. [11] From the results of cell size and compressive strength of the PUFs shown in Figure 2-14 and Figure 2-16, it is suggested that the increase of compressive strength of the PUFs with the perfluoroalkane can be explained by the smaller cell size. For the PUFs prepared with propylene ecarbonate, the compressive strength was found to be 1.230, 1.320, and 1.305 MPa for the additive content of 0.0, 1.0, and 2.0 php, respectively.

Density of the PUFs did not change greatly with the increase of the propylene carbonate, which was 115.2, 114.1, and 113.7 kg/m^3 when the propylene carbonate content was 0.0, 1.0, and 2.0 php, respectively (Table 2-8). The slight increase of compressive strength of the PUFs with the propylene carbonate is possibly because the propylene carbonate acts as a chain extender in the preparation of the PUFs. However, the compressive strength of the PUFs with the acetone decreased from 1.230 to 0.855 MPa when the acetone content increased from 0.0 to 2.0 php. The decrease in compressive strength of the PUFs with acetone is mainly due to the

decrease of densities from 115.2 to 94.3 kg/m^3 when the acetone content increases from 0.0 to 2.0 php, which are shown in Table 2-8. Figure 2-18 shows the relationship between the compressive strength and density of the PUFs with the three different additives (perfluoroalkane, propylene carbonate and acetone). Compressive strength of the PUFs with the three different additives is increased with the increase of density of PUFs. Mechanical properties of the rigid PUFs depend mainly on the density of the foams. For the PUFs with the acetone, the cells seemed coalesced because of the larger cell size compared to those of the foams with the perfluoroalkane and propylene carbonate. This caused less density and consequently less compressive strength of the PUFs with the acetone. [14]

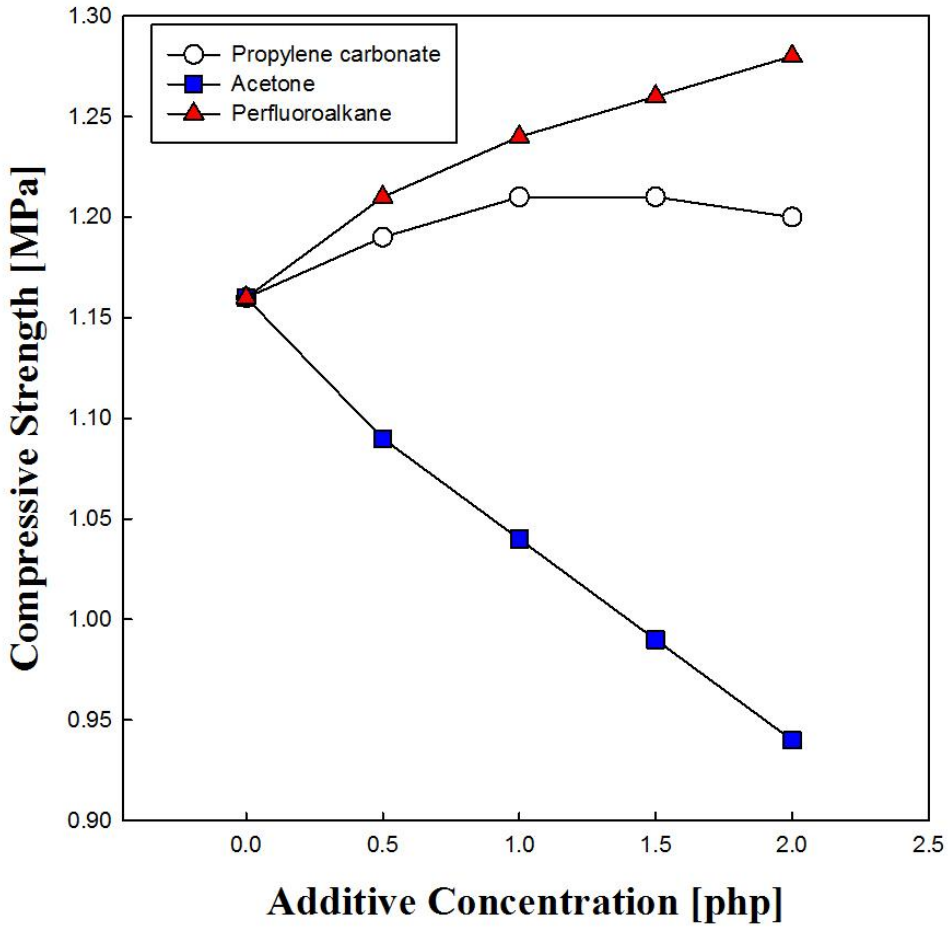


Figure 2-17. Compressive strength of PUFs with various additives at different concentrations [14]

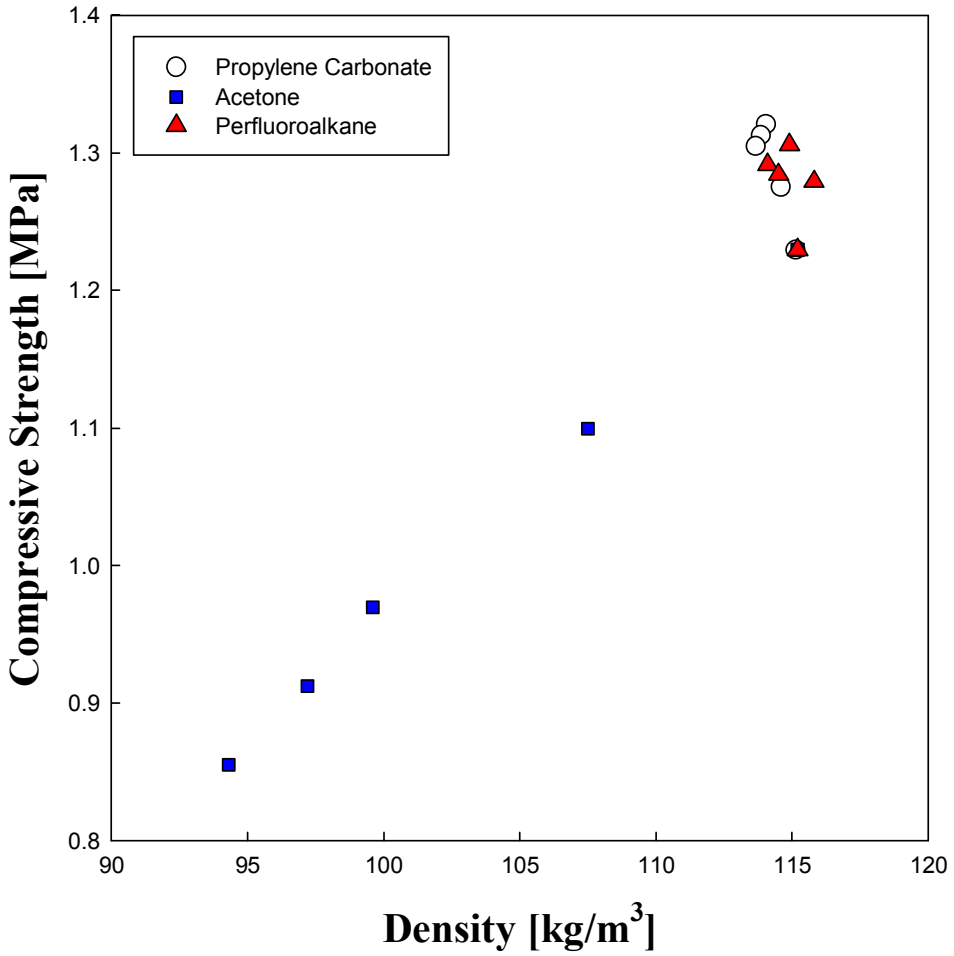


Figure 2-18. Relationship between compressive strength and density of PUFs with various additives at different concentration [14]

CHAPTER 3 : Construction of Blending System for Commercial Mass Production Type PUF

3.1. Introduction

In chapter 2, the morphology, thermal conductivity, and mechanical strength of PUFs with the three liquid-type additives (perfluoroalkane, propylene carbonate, and acetone) were investigated. From the results of the morphology and the thermal properties of the PUFs, it is suggested that foams prepared with perfluoroalkane were characterized by smaller average cell diameter and lower thermal conductivity compared with the PUFs that were prepared with propylene carbonate or acetone. The addition of perfluoroalkane seems to induce smaller cell size, probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate of the PUFs.

From the results of compressive strength of the PUFs, it is suggested that the increase of compressive strength of the PUFs with the perfluoroalkane can be explained by the smaller cell size of the foams. The smaller cell size appears to be an important reason for the improvement of thermal insulating and mechanical properties of PUFs. The results of morphology, thermal conductivity, and compressive strength of the PUFs suggest that perfluoroalkane may be the efficient liquid-type additive for the improvement of the thermal insulation property of the PUFs. [14]

A conventional LNG carrier need more than 15,000 insulation panel and over 6,000 m^3 polyurethane foam. So the blending system for mass production type

polyurethane foam should be developed based on the lab and bench scale test results. In order to manufacture rigid PUF under mass production environment, in which amount of raw materials is 10,000 times larger than that of raw materials in a laboratory scale, optimum amount of PFA and blowing agent were searched again in such a way to decrease thermal conductivity and to increase compressive strength. In addition, since rigid PUFs manufactured in an industrial continuous line should be aged at room temperature for more than 7 days after synthesis, aging characteristics of rigid PUFs was also considered. [13]

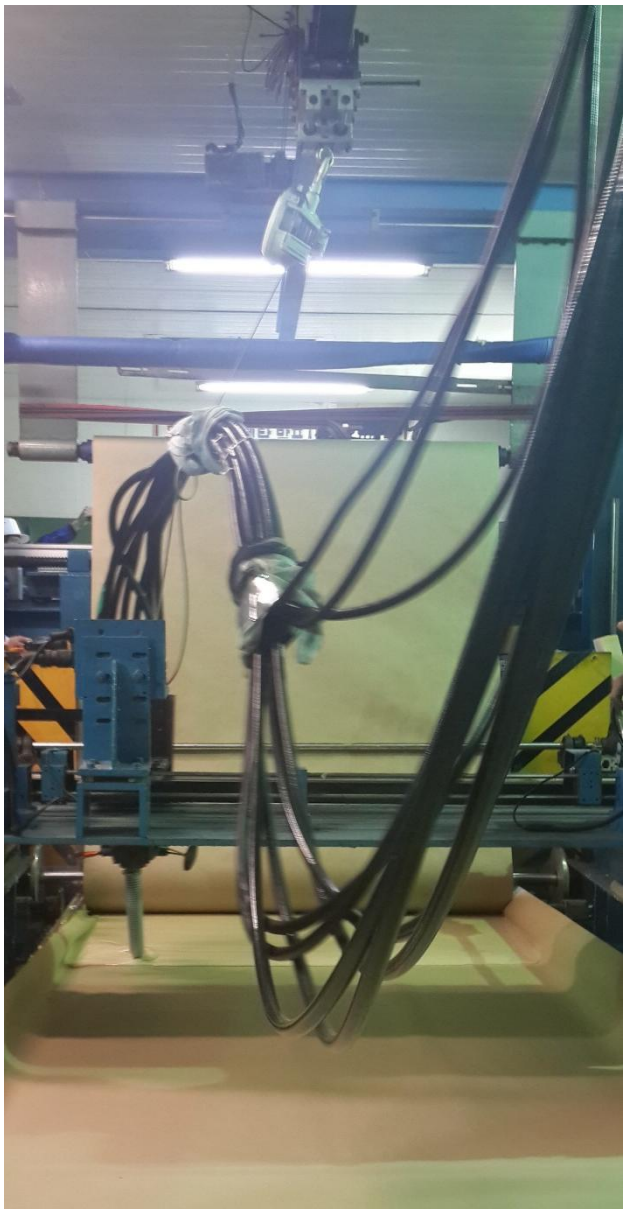


Figure 3-1. Production of polyurethane foam using a continuous production line

3.2. Blending system for mass production type polyurethane foam

A raw material blending system for mass production of polyurethane foam was formulated and the blending system was improved while producing PUF in the continuous commercial production line. The blending system was finally fixed through this correction process.

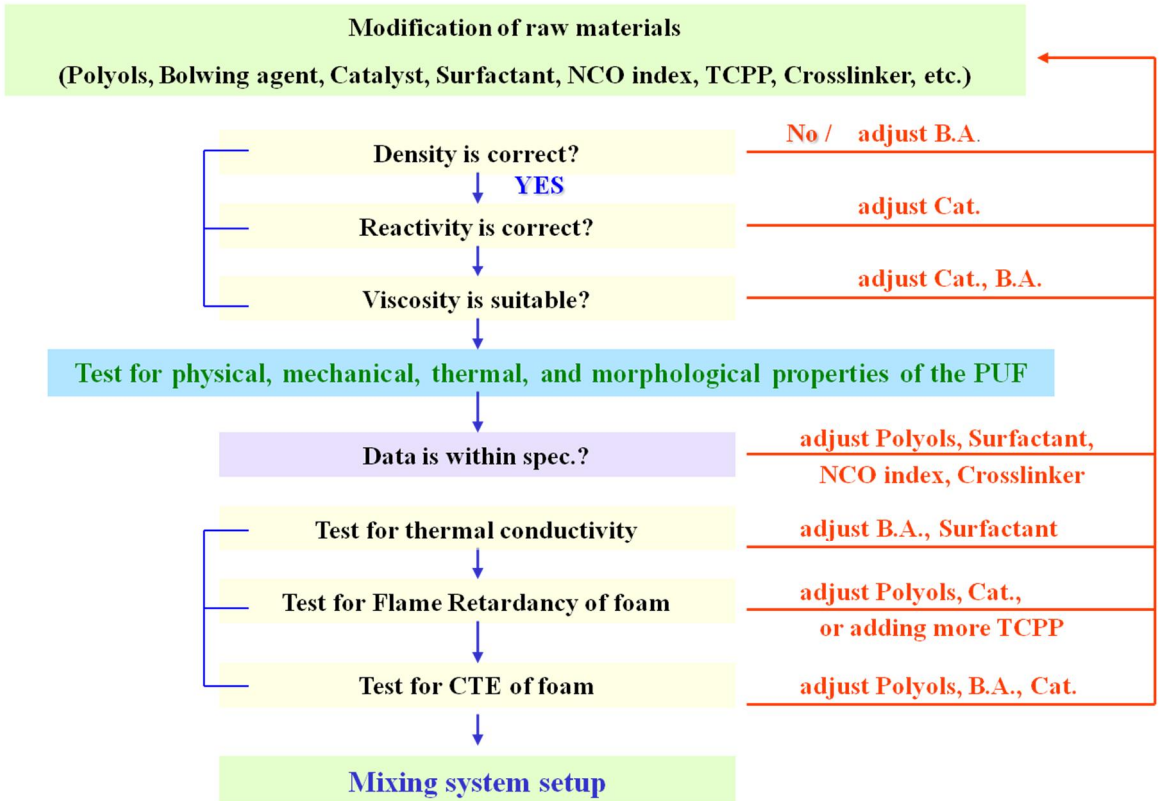


Figure 3-2. Flow chart for blending system setup procedures

Table 3-1. Optimizing of blending system for mass production type polyurethane foam

System No.	LT 1440/2	LT 1440/6	LT 1440/9	LT 1440/14
Polyester polyols	50	40	50	45
Polyether polyols	40	56	45	48
Chain extending agent	10	4	5	7
Catalysts	2.23	2.37	2.36	2.35
Perfluoroalkane	-	-	1.0	0.5
HFC-365mfc	7.2	7.6	7.0	
HFC245fa				7.7
Density [kg/m^3]	126	127	126	119
Gel. Time [second]	330	285	275	270
Compressive Strength [MPa]	1.33	1.24	1.20	1.21
Thermal conductivity @20^oC [mW/mK]	23.2	25.3	23.7	22.4

Table 3-2. Problems encountered during the optimization process and remedied [13]

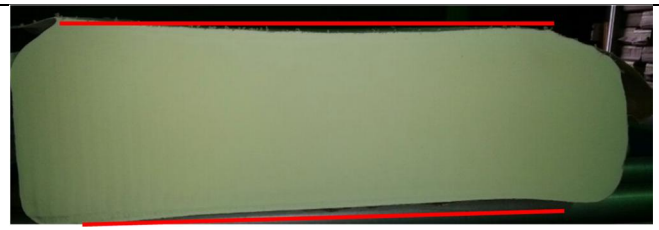
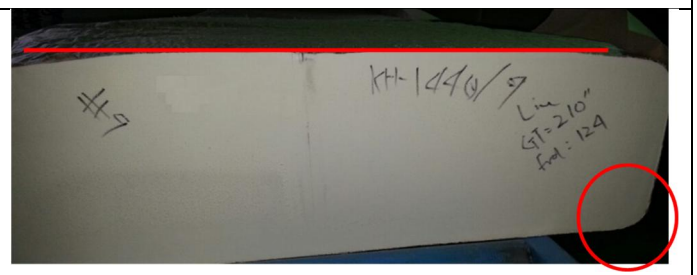
Reasons for correction	Related picture
LT 1440/2 system Bad flowability and poor shape of foam block → adjusting reactivity and facilitating release of reaction heat by adjusting polyol composition	
LT 1440/6 system No swelling Corner shape and thermal conductivity need improvement → use perfluoroalkane and adjusting polyol composition	

Table 3-3. Problems encountered during the optimization process and remedies [13]

Reasons for correction	Related picture
LT 1440/9 system No swelling. Corner shape was improved but thermal conductivity needs improvement → change amount of perfluoroalkane, adjust polyol composition and change blowing agent to HFC-245fa	
LT 1440/14 system No swelling Corner shape and thermal conductivity were improved. Blending system was finally fixed.	

3.3. Conclusion

The problems that occur in each system and the improvement process that reflects them are shown in Table 3-1 to Table 3-3. During optimization process the blending system was adjusted to remove swelling phenomena, improve the block corner shape, and thermal conductivity etc. by changing polyol composition, and reactivity and adding perfluoroalkane etc. And the blending system for mass production type polyurethane foam was finally fixed. In the next section, we will use the confirmed blending system to produce and evaluate the insulation material, so that we can confirm the possibility of using LNG carrier of mass-produced polyurethane foam insulation.

CHAPTER 4 : Evaluation and Confirmation of the Possibility of Using the Mass-produced Polyurethane Foam Insulation for a LNG Carrier

4.1. Introduction

In chapter 3, the blending system for mass production type polyurethane foam was fixed. Now we produce polyurethane foam by using commercial continuous production line and evaluate the properties to confirm the possibility of using the mass-produced polyurethane foam insulation for a LNG carrier. Before evaluation, rigid PUFs manufactured in an industrial continuous line should be aged at room temperature for more than 7 days after synthesis, aging characteristics of rigid PUFs was also considered. [13]

(a)

(b)

Figure 4-1. Production of polyurethane foam using a continuous line; (a) discharge of mixture, (b) foamed block

Figure 4-2. Stabilization of polyurethane foam block at ambient temperature

4.1.1. Heat transfer in conjugated membrane type insulation panel

An insulation panel for LNG carriers has a conjugated structure in which rigid PUF layer is located between upper and lower birch plywoods. In this structure, heat transfer rate can be described in Eq. (2).

$$Q = S(T_h - T_c)/(d_{tot}/\lambda_{tot}) \quad (2)$$

where

$d_{tot}/\lambda_{tot} = d_{ply1}/\lambda_{ply1} + d_{PUF}/\lambda_{PUF} + d_{ply2}/\lambda_{ply2}$

Q = heat leakage rate through the insulation panel in W

d_{tot}= thickness of insulation panel

d_{ply1} = thickness of the upper plywood

d_{PUF} = thickness of PUF insulator

d_{ply2} = thickness of the lower plywood

λ_{tot} = total effective thermal conductivity in W/m K

λ_{ply1} = effective thermal conductivity of the upper plywood in W/m K

λ_{PUF} = effective thermal conductivity of PUF in W/m K

λ_{ply2} = effective thermal conductivity of the lower plywood in W/m K

T_h = temperature of the hot surface in K

T_c = temperature of the cold surface in K

S = area perpendicular to heat flow in m^2

Since the thermal conductivity of plywood (200 mW/m K at 20 ^oC) is generally much higher than that of PUF (24 mW/m K at 20 ^oC) but the thickness of plywood

is very small (usually less than one tenth) in comparison with that of PUF layer, total heat flux through the insulation panel relies mainly on the characteristics of PUF [2, 13, 43-45].

In order to synthesize PUF with low apparent thermal conductivity, small size of cell structure and low foam density turn out to be preferred [8, 46, 47]. These characteristics can be achieved by homogeneous mixing of raw materials and resultant uniform reaction. Thus, mixing condition and role of additives should be considered in designing PUF for LNG carriers. [13]

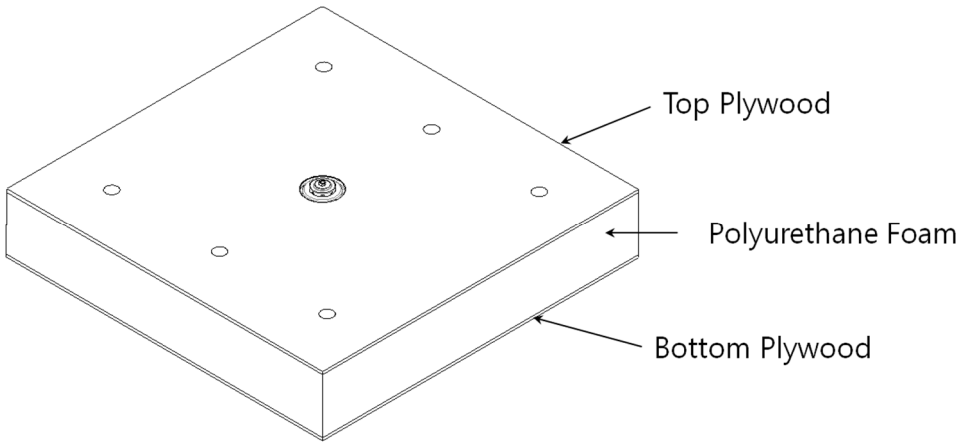


Figure 4-3. A basic insulation panel for a LNG cargo containment system and its components [2, 14]

Table 4-1. Resistance of each component of insulation panel forKC-1 CCS

Insulation Panel	Upper Plywood	Polyurethane Foam	Lower Plywood
Density [kg/m^3]	630	118	630
Thickness [m]	0.012	0.2325	0.012
Thermal Conductivity [mW/mK]	200	24	200
Resistance [m^2K/W]	0.0600	9.6875	0.0600
Relative Resistance with $R_{PUF} = 1.0$	0.0062	1.0000	0.0062

4.1.2. Calculation of boil-off rate in LNG carrier

Boil-off rate (BOR) in LNG carrier is calculated by using Eq. (3) under the assumption that the cargo containment is filled to 98% with pure methane (CH_4) and the temperatures of external air and seawater are 45 ^{o}C and 32 ^{o}C, respectively.

$$\text{Boil-off rate [\%/day]} = \frac{Q_T \times 24 \times 100}{V \times \rho \times L_m} \quad (3)$$

Where,

Q_T = Total heat transfer rate in kJ/h

V = Cargo capacity (full loading, 98% of the total volume) in m^3

P = Pure methane density, 425 kg/m^3

L_m = Vaporization latent heat of the methane, 512 kJ/kg

Total heat transfer rate (Q_T) in Eq. (2) is obtained from Eq. (3) under the assumption that the insulator panel experiences temperature difference between -160 ^{o}C (LNG-side surface temperature) and 20 ^{o}C (seawater-side surface temperature). [13]

4.2. Measurement and experimental conditions

Thermal conductivity Curve

The thermal conductivity from -160 ^{o}C to 20 ^{o}C was measured by using Titan of Netzsch for two identical 300 mm x 300 mm x 25 or 30 mm samples in accordance with the Guarded Hot Plate (GHP) test method ISO 8302 (ASTM C177). Temperature difference was every 20 ^{o}C at all set points. The test bath was evacuated for 30 min and filled with nitrogen gas, which was repeated three times to remove any vapor and to avoid icing. [13] Guarded hot plate method effectively prevent lateral heat flow through several guard heaters even under abnormal atmosphere. So GHP method is an appropriate test method for measuring thermal conductivity under cryogenic temperature range.

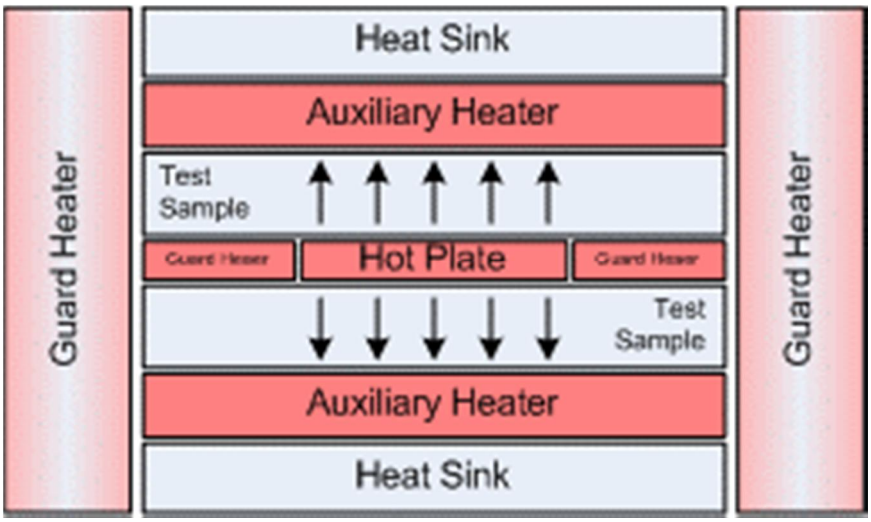
Mechanical Properties at Low Temperature

In order to measure mechanical strength, Instron UTM 4467 was employed. Especially for low and cryogenic temperature measurement, a cryogenic chamber in Figure 4-5 was employed. In this case, samples were dipped in a liquid nitrogen container for one hour and then installed with a test jig in the cryogenic chamber. For tensile strength measurement at low or cryogenic temperature, samples were prepared in the shape shown in Figure 4-5 in order to prevent slippery at a test jig. The measurement was made in accordance with test method ISO 1926 except for using dog-bone shape specimens. Crosshead speed was 5.0 mm/min. Shear strength was measured with 50 mm x 50 mm x 5mm specimens in accordance with test method ASTM D732. Crosshead speed was 1.25 mm/min. Compressive strength was measured with 50 mm x 50 mm x 50 mm specimens in accordance

with test method ASTM D1621. Crosshead speed was 5.0 mm/min. [13]

Thermal Stability at Low Temperature

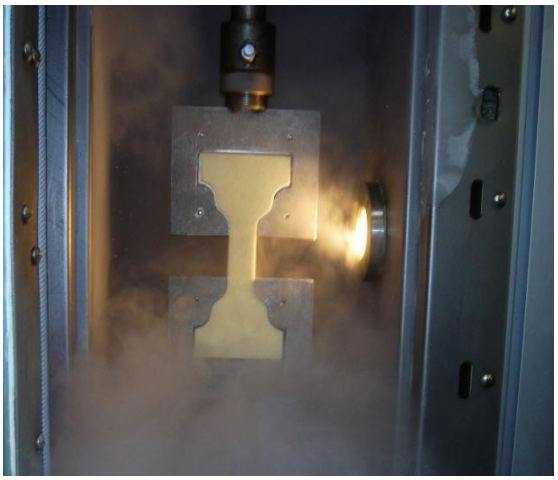
In order to check thermal stability of PUFs, coefficient of thermal expansion (CTE) from cryogenic to room temperature was measured using a dilatometer from NETZSCH (model: DIL 402C with 414/4). The measurement follows the ASTM E228 procedures with heat rate of 5 ^{o}C /min. In addition, thermal shock test was done by preparing a test sample like that shown in Figure 4-7. The test sample was thermally shocked three times, which was done in such a way to dip it in a liquid nitrogen container for one hour and to put it at atmosphere temperature for two hours. After these thermal shocks, the sample was investigated to check if there occurs crack or delamination by the thermal expansion mismatch among PUF, plywood and adhesive. [13]



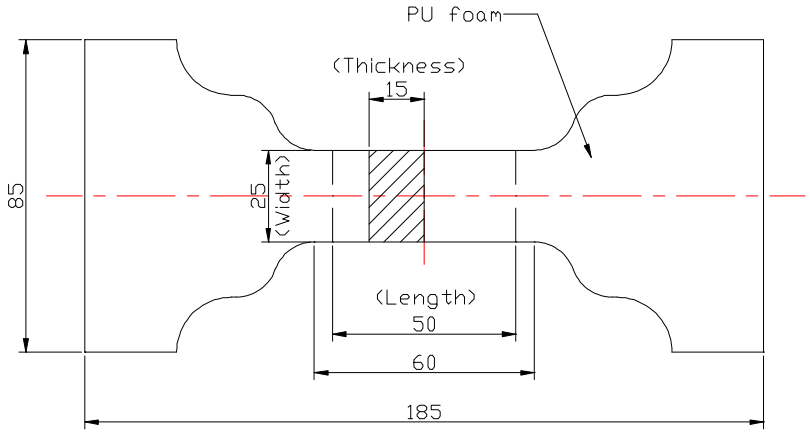
(a)

(b)

Figure 4-4. Guarded Hot Plate Method; (a) schematic diagram of basic theory, (b) Titan of Netzsch [13]

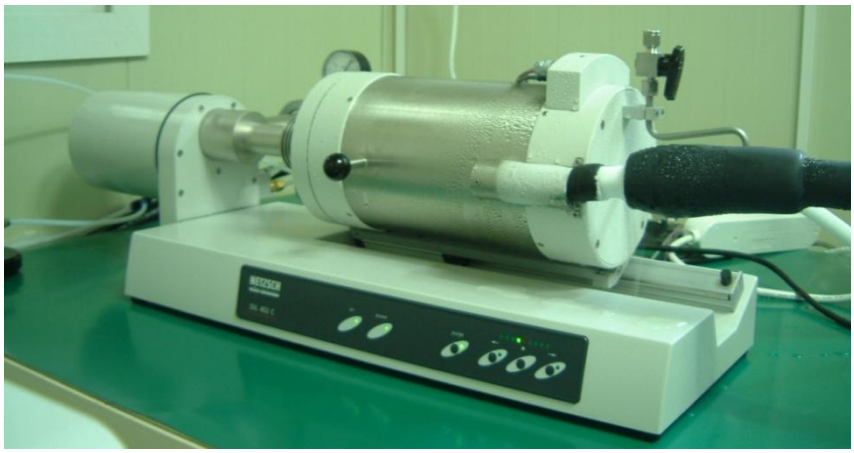


(a)

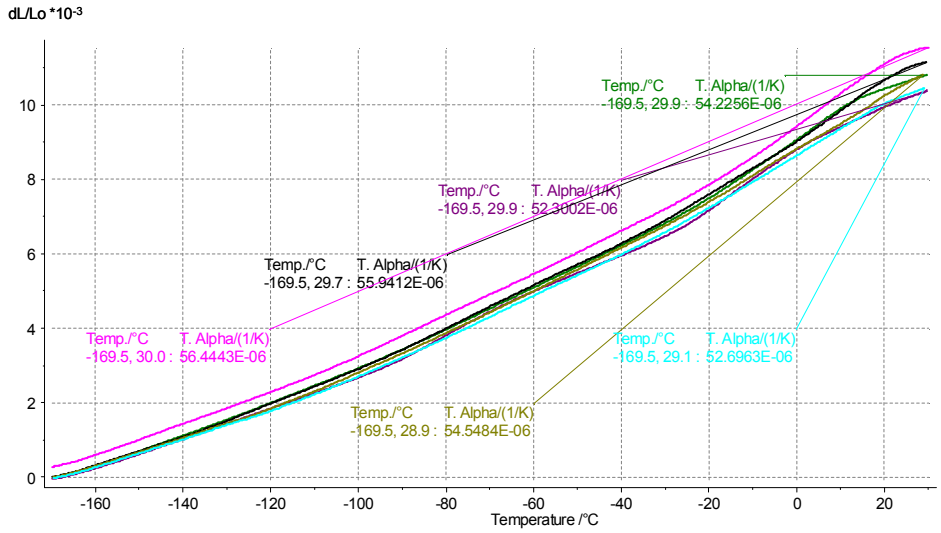


(b)

Figure 4-5. Mechanical strength test; (a) cryogenic chamber, (b) sample shape for tensile strength [unit: mm] [13]



(a)



(b)

Figure 4-6. Machine for measuring CTE; (a) dilatometer, (b) typical test-result graph

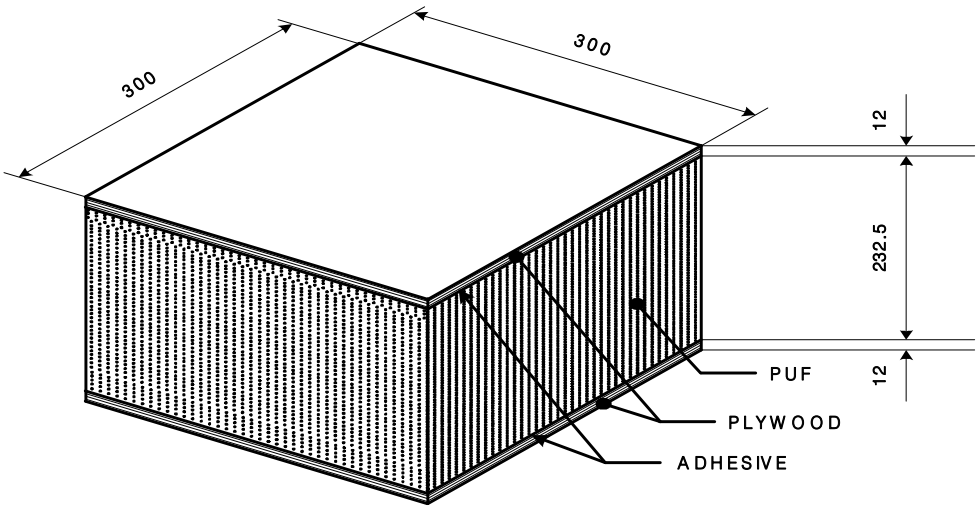
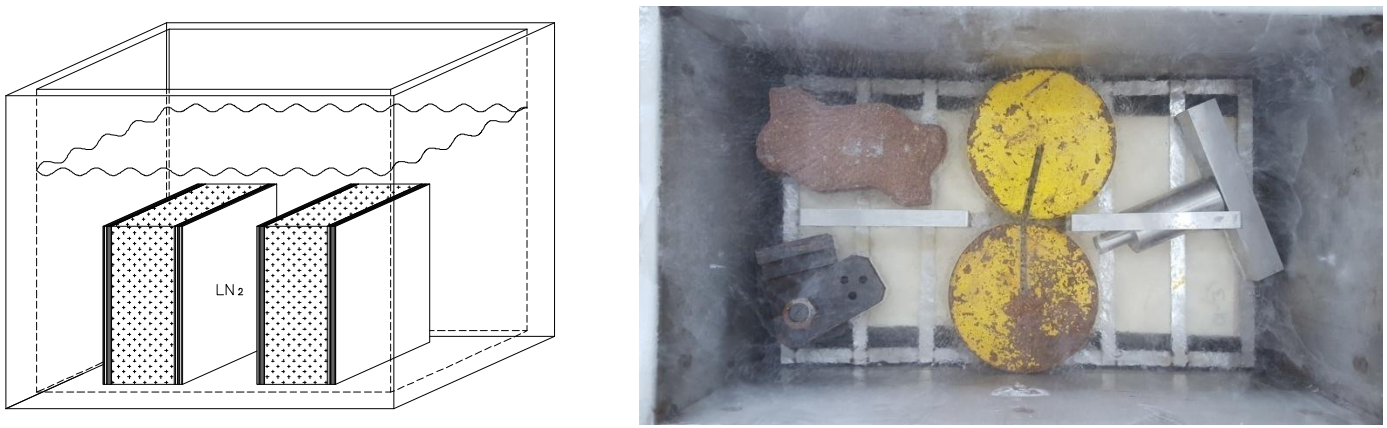


Figure 4-7. Structure of sample for thermal shock test [unit: mm] [13]



(a) (b)

Figure 4-8. Thermal shock test; (a) schematic diagram, (b) real test [13]

Note: The yellow round steel, black steel etc. are materials to maintain the samples to be dipped in LN2

4.3. Evaluation results

The mass-produced polyurethane foam was used to evaluate whether it could be applicable to a LNG carrier. Three types of tests were performed for this purpose. One is the mechanical strength test, the other is the insulation performance test of the insulation, and the other is the stability test in the actual operating environment.

4.3.1. Mechanical strength characteristics

Table 4-2 summarizes mechanical strength specifications of the PUF for a conventional LNG carrier. Compressive strength of PUF in a height direction should be larger than 0.95 MPa at 25 ^{o}C and 1.23 MPa at -170 ^{o}C, respectively. Tensile strength of PUF in both length and width directions should be larger than 1.00 MPa at 25 ^{o}C and 1.15 MPa at -170 ^{o}C, respectively. Shear strength of PUF in every length, width and height directions should be larger than 0.7 MPa at 25 ^{o}C and at -170 ^{o}C. Table 4-2 shows the results of the mass produced PUF blown by HFC-245a with PFA addition. The measurement was made by the method described in Chapter 2-3. It is shown that the mechanical strengths at 25 ^{o}C and at -170 ^{o}C for the PUF meet the specification in Table 4-2.

Table 4-2. Specification of PUF for a conventional LNG carrier [13]

Item	Compressive strength[a] [MPa]		Tensile strength[b] [MPa]		Shear strength[c] [MPa]	
Temperature [^{o}C]	25	-170	25	-170	25	-170
Specification	≥ 1.10	≥ 1.50	≥ 1.20	≥ 1.40	≥ 0.8	≥ 0.8

[a] In height direction

[b] In length and width directions

[c] In height, length and width directions

Table 4-3. Mechanical strengths of mass produced PUF blown by HFC-245fa with PFA addition over various temperatures [13]

Temperature [^{o}C]	Compressive strength [MPa]	Tensile strength [MPa]		Shear strength [MPa]		
Direction	Height	Length	Width	Length	Width	Height
25	1.25	1.24	1.21	0.84	0.87	0.83
-50	1.53	1.78	1.69	0.95	0.95	0.96
-100	1.86	2.01	2.01	1.08	1.03	1.14
-170	2.12	2.39	2.49	1.13	1.19	1.23

4.3.2. Thermal conductivity characteristics

Figure 4-9 shows the apparent thermal conductivity curve between -160 ^{o}C and 20 ^{o}C for mass production type PUFs. Here, HFC-245fa only indicates a PUF blown by HFC-245fa and HFC-245fa + PFA indicates a PUF by HFC-245fa with PFA additive. Both samples were aged for more than 4 months at a temperature of 25 ± 5 ^{o}C before measurement. The HFC-245fa + PFA case shows lower thermal conductivity than the HFC-245fa only case. For the HFC-245fa + PFA case, the effective (average apparent) thermal conductivity between -160 ^{o}C and 20 ^{o}C is 18 mW/m K and for the HFC-245fa only case, it is 19 mW/m K. The effective thermal conductivity was calculated by using the fit curve for the measured values between -160 ^{o}C and 20 ^{o}C.

With these effective thermal conductivities, BOR was calculated from Eq. (3) in Section 4.1.2. The calculated BOR for the HFC-245fa + PFA case is lower than 0.12%/day, which meets the BOR specification for a conventional LNG carrier. [13]

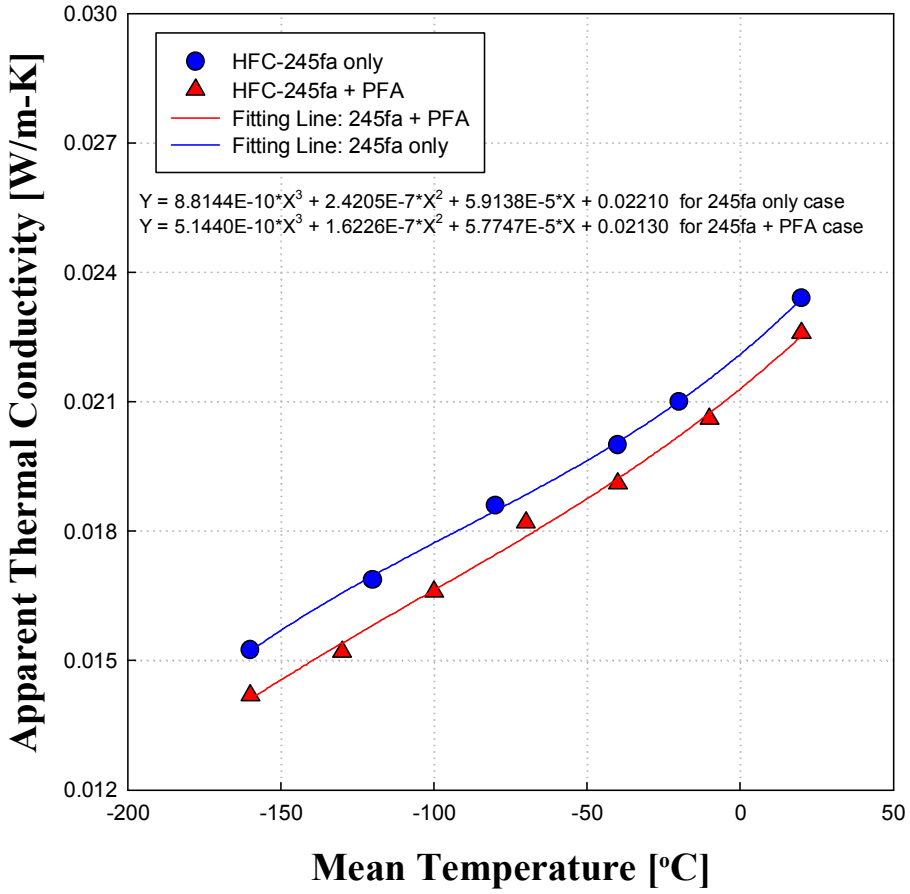


Figure 4-9. Apparent thermal conductivity curves of mass production type PUFs [13]

4.3.3. Thermal stability characteristics

Coefficient of thermal expansion (CTE) of the mass production type PUF should be lower than 60 x 10^{-6} [1/K] over the temperature range between -170 ^{o}C and 25 ^{o}C so that it can maintain thermal insulating performance without any severe volume change. [13]

The measured CTE values of the mass production type PUF were summarized in Table 4-4. The CTE values of each direction are very close to one another. This indicates that cells in the PUF have spherical shape so that thermal load from low temperature can be distributed uniformly. In addition, it can be seen that relative shrinkage amount of the PUF decreases as temperature goes down. Of course, CTE of the PUF is low enough to meet the specification for a conventional LNG carrier.

As another test item, thermal shock was applied to an insulation panel, which was prepared like that described in Section 3.1. As shown in Figure 4-8, there is no damage of the test species after three cycles of thermal shock test.

Table 4-4. Coefficient of thermal expansion for the mass production type PUF blown by HFC-245fa with PFA addition [13]

Temperature range [^{o}C]	CTE / length dir. X10^{6} [1/K]	CTE / width dir. X10^{6} [1/K]	CTE / height dir. X10^{6} [1/K]
From -50 to 25	66.93	63.88	66.49
From -100 to 25	62.30	61.46	61.86
From -170 to 25	54.62	54.81	54.27
Specification from -170 to 25	≤ 60.0	≤ 60.0	≤ 60.0

4.4. Lifetime Evaluation of Polyurethane Foam

Polymer foam can not recover to its original state when it is subjected to a load exceeding the yield strength or a deformation more than the yield strain. The yield strength and the yield strain of polyurethane foam can be calculated from the stress-strain graph when measuring compressive strength. When a constant load is continuously applied to a polymer material, the strain is increased even though the load is not increased, and this phenomenon is called a creep. The prediction of strain by creep can be calculated by the following Findley's equation. [48]

$$\varepsilon_t = \varepsilon_0 + \varepsilon_c = \varepsilon_0 + m \times t^n \quad (4)$$

Where,

ε_t = total strain at time t after a stress application,

ε_c = the time-dependent (creep) component of strain at some time t after a stress application,

ε_o = immediate strain upon a stress application

m = dimensionless material parameter

n = dimensionless material parameter

t = time in hour

The time at which the creep strain of the polyurethane foam used reaches the yield strain of compression is defined as the lifetime. The load-length of change curve of the polyurethane foam produced by the new blending system can be seen in the

following figure. The size of samples used was 50 mm x 50 mm x 50 mm (width x length x thickness).

LNG carrier will be filled to more than 95% when loading LNG from the production site to the demand site. On the other hand, when LNG is unloaded from the demand site and returned to the production site, LNG is filled less than 10%. However, in order to calculate the lifetime, it is assumed that the polyurethane foam is always under the design load (0.33 Mpa) during the whole lifetime. The strain rate of the polyurethane foam was calculated and the results are shown in the following table. Consequently, the strain of the polyurethane foam, which is expected to occur after 25 years, is about 2.0%, which is smaller than the yield strain of 2.8 %. The predicted creep life of the polyurethane foam is about 104 years.

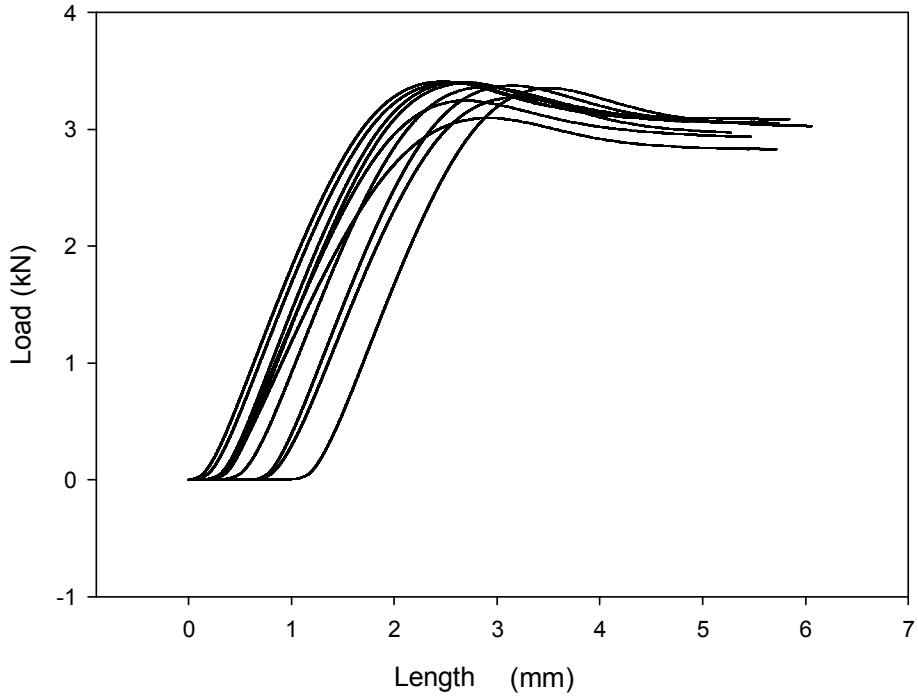


Figure 4-10. Graph of load-length change of compressive strength of PUFs

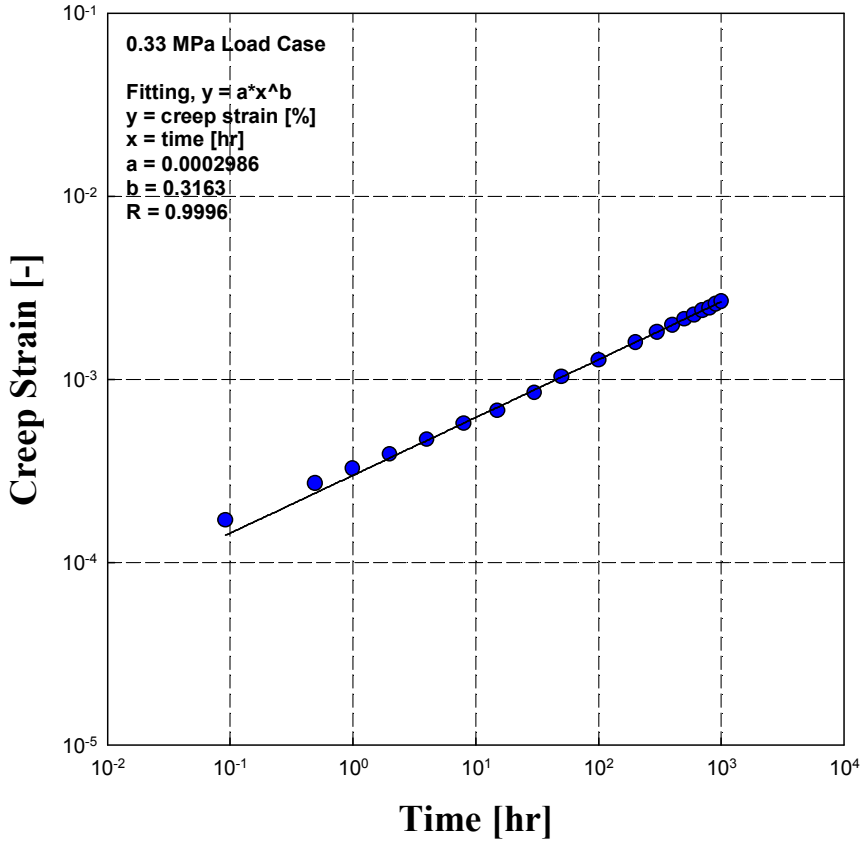


Figure 4-11. Analysis of creep data of PUF (0.33 MPa)

Table 4-5. Analysis of creep test

Load [MPa]	Yield strain [%]	Initial strain [%]	Findley's coefficient		Life time [year]	Strain after 25 years [%]
			m	n		
0.33	2.8	0.511	0.00030	0.3163	104	1.97

4.5. Economics

Prior to the actual application of the new blending system to a LNG CCS, the economics was compared for the case with and without additives considering the difference of insulation performance and the difference of the thickness of insulation. Due to the addition of expensive additives, the price of the new system using perfluoroalkane is higher than the price of the old system without profluroalkane as shown in Table 4-6. But the equivalent thickness of the new system is thinner than the one of the old system thanks to lower effective thermal conductivity. Considering these together, the total application price of the new system is lowered due to the outstanding thermal insulating performance.

Table 4-6. Cost comparison between the old PUF blending system and the new one.

Component		Unit price KRW/kg	Old blending system		New blending system	
			Amount [kg]	Cost [KRW]	Amount [kg]	Cost [KRW]
A-Liq.	Polyols	3,200	89.2	285,340	88.8	284,318
	Surfactant	9,000	1.8	16,050	1.8	15,993
	Catalyst	9,000	2.1	18,860	2.1	18,792
	HFC-245fa	14,000	7.0	97,370	6.8	95,780
	Perfluoroalkane	60,000	0		0.4	26,655
	Sum		100.0	417,610	100.0	441,537
	Unit price [KRW/kg]			4,176		4,415
B-Liq.	Polymeric MDI	2,500	100	250,000	100	250,000
	Unit price [KRW/kg]			2,500		2,500
Unit price of blending system [KRW/kg]				3,338		3,458

Table 4-7. Approximate cost comparison between the old PUF blending system and the new one about application to a 170K LNG carrier [2].

Item	Old system	New system
Density of PUF [kg/m^3]	119	119
Average effective thermal conductivity of PUF between -160 ^{o}C and 20 ^{o}C [mW/mK]	19	18
Thickness [m]	0.2454	0.2325
Total raw material amount [ton/170K ship]	1,481	1,403
Total raw material cost [million KRW]	4,944	4,852

4.6. Conclusion

As mentioned, the mass-produced polyurethane foams were evaluated about the possibility of adaptation to a conventional LNG carrier. The evaluation was performed in three sections; mechanical strength, insulating performance, thermal stability at operating conditions. We also found that the new system using perfluoroalkane is more economical in terms of price than the old system without additive. Judging from the results so far, it is believed that the mass production type PUF blown HFC-245a with PFA addition can be applied to a thermal insulator for a conventional LNG carrier. [13]

CHAPTER 5 : Concluding Remarks

5.1. Conclusions

In this study, the morphology, thermal conductivity, and mechanical strength of PUFs with the three liquid-type additives (perfluoroalkane, propylene carbonate, and acetone) were investigated. As one of the additives, polypropylene carbonate (PC) shows 8.6% increase of compressive strength but meaningless effects on density and thermal conductivity when amount of PC is added up to 1.5 php. As another additive, acetone shows 28% decrease of compressive strength and 15% decrease of density but slight increase of thermal conductivity when amount of acetone is added up to 2 php. As the other additive, PFA shows dramatic change of rigid PUF properties such as 5% decrease of compressive strength, 11% decrease of thermal conductivity, and 10% decrease of density when amount of PFA is added up to 2 php. This dramatic change is valuable to further optimize PFA effects, which results in 12% decrease of thermal conductivity and 15% increase of compressive strength. This result was obtained by adjusting amount of PFA as well as that of blowing agent. [13, 14]

From the results of the morphology and the thermal properties of the PUFs, it is suggested that foams prepared with perfluoroalkane were characterized by smaller average cell diameter and lower thermal conductivity compared with the PUFs that were prepared with propylene carbonate or acetone. The addition of perfluoroalkane seems to induce smaller cell size, probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate of the PUFs. From the results of compressive strength of the PUFs, it is suggested

that the increase of compressive strength of the PUFs with the perfluoroalkane can be explained by the smaller cell size of the foams. The smaller cell size appears to be an important reason for the improvement of thermal insulating and mechanical properties of PUFs. The results of morphology, thermal conductivity, and compressive strength of the PUFs suggest that perfluoroalkane may be the efficient liquid-type additive for the improvement of the thermal insulation property of the PUFs. [13, 14]

In order to manufacture mass production type rigid-PUF for LNG carriers using ozone depletion free blowing agents, effects of additives on the properties of rigid-PUF were evaluated in a laboratory scale, first. Based on the result in the laboratory scale, mass production type rigid PUF (HCFC-245fa + PFA) using an ozone depletion free blowing agent was manufactured. The effective thermal conductivity of the mass production type rigid PUF between -160 ^{o}C and 20 ^{o}C is 0.0180 W/mK and it satisfies the BOR specification, 0.12%/day, without violating mass production requirements. The mass production type rigid PUF also shows enough mechanical strengths and thermal stability for the LNG carrier's operation temperature. Thus it can be said that the mass production type PUF blown by HFC-245a with PFA addition is utilized as a thermal insulation material for a conventional LNG carrier. [13, 14]

Finally, the results of the quantitative and qualitative effects of the additives in this study can be expected to play a important role in reducing the time and efforts required to construct a new blending system for improving the insulation performance and physical properties in the future by changing the foaming agent.

5.2. Future works

It is predicted that substantial regulation of global warming materials will be in effect soon, as the world is currently experiencing global weather disasters due to climate change. The third-generation blowing agents, HFCs, have zero ODP but large GWP. Therefore, it is predicted that HFCs will be banned in the near future, and the 4th generation blowing agents, which have no ODP and almost no GWP at the same time, are on the market. In order to maintain the competitiveness of the LNG carrier cargo containment system, the insulation performance and mechanical performance must be secured even in the new blending system using the new fourth-generation blowing agent. On the basis of the results obtained in this study, the development of the polyurethane foam blending system using the fourth generation blowing agents should be continuously carried out in the new projects to be carried out with this purpose.

Nomenclature

Greek letters

λ	effective thermal conductivity
θ	contact angle
$\emptyset$	ratio of molar volume of liquid and solid
γ	surface energy

Subscripts

c	cold surface
h	hot surface
L	liquid
m	methane
S	solid
T	total

Abbreviations

BOR	Boil-off rate
CCS	Cargo containment system
CFCs	Chlorofluorocarbons
CFC-11	Trichlorofluoromethane

CTE	Coefficient of thermal expansion
CHP	Guarded hot plate
GWP	Global warming potential
HFM	Heat flow meter
HCFCs	Hydrochlorofluorocarbons
HCFC-141b	1,1-dichloro-1-fluoroethane
HFCs	Hydrofluorocarbons
LNG	Liquefied natural gas
NG	Natural gas
ODP	Ozone depletion potential
PC	Propylene carbonate
PFA	Perfluoroalkane
php	parts per hundred polyols by weight
PUF	Polyurethane foam
SEM	Scanning electron microscope

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Abstract in Korean (요 약)

폴리우레탄은 폴리올과 이소시아네이트의 발열반응에 의해 만들어지는 고분자 물질이다. 폴리우레탄은 그 우수한 특성으로 인하여 많은 산업분야에서 널리 사용되고 있다. 특히 경질 폴리우레탄은 가장 우수한 단열재 중 하나이며 그 뛰어난 단열 성능으로 인하여 LNG 저장탱크, LNG 수송선과 같은 초저온 설비용 단열재로 사용되고 있다.

발포제는 폴리우레탄을 셀구조로 만들며 폴리우레탄폼에 단열성능을 제공하는 물질이다. HCFC-141b는 CFCs를 대체하는 발포제로 사용되어 왔다. 하지만 ODP가 0.11로 CFCs에 비해 작기는 하지만 이 또한 오존층을 파괴하는 물질로 HFCs와 같은 ODP가 없는 3세대 대체 발포제로의 대체가 요구된다.

LNG 산업은 특성상 폴리우레탄 폼과 같은 높은 단열성능을 갖는 자재의 사용이 요구되는 분야이다. 근래 들어 LNG 가격이 높아지고 LNG 수송선 추진시스템의 효율이 높아져 LNG 선박의 주요 사양 중 하나인 증발가스생성율(BOR)이 낮아지고 있다. 즉, 125,000 m^3에서 170,000 m^3 규모를 갖는 LNG 수송선의 BOR 사양이 종래 0.15%/day에서 0.12%/day로 낮아진 것이다. 이렇게 엄격해진 BOR 사양은 HCFC-141b로 제조된 폴리우레탄폼(PUF)을 사용함으로서 만족시킬 수 있다. 하지만 엄격해진 환경규제로 인하여 HCFC-141b를 사용할 수가 없기 때문에 이의 환경친화적 발포제로의 대체가 이루어져야 한다. 이러한 대체발포제의 사용은 환경친화적이기는 하지만 발포제 자체의 열전도도가

높기 때문에 생산된 PUF의 단열성능이 떨어지게 되는 단점이 있다.

본 연구에서는 HCFC-141b의 대체발포제로서 HFCs를 검토하고 단열성능 저하를 보상하기 위한 액상첨가제 사용을 점검하고 생산된 PUFs의 특성과 LNG 수송선에의 적용 적합성을 확인해보고자 한다. 우선 저하되는 물성의 보완을 위하여 몇 가지 첨가물질을 도입, 실험실 규모에서 그 성능 개선 가능성을 확인하였다. 또한 이러한 결과를 상업규모로 대량 생산할 PUF 조성에 적용하고자 한다. 우선, 세 가지 액상 첨가제로서 프로필렌 카보네이트(PC)와 아세톤, 과불화알칸(PFA)의 사용을 검토하였다. 세가지 액상 첨가제를 도입하여 제조한 PUFs의 점검 결과 PFA를 도입하여 제조한 PUF의 셀은 PC나 아세톤을 도입하여 제조한 PUF의 셀보다 작았으며 더 낮은 열전도도를 나타냈다. PFA를 사용하여 제조한 PUFs는 PC나 아세톤을 사용하여 제조한 PUFs보다 우수한 단열성능과 높은 기계적 강도를 나타내었으며 이로부터 PFA는 PUF의 성능을 향상시킬 수 있는 효과적인 액상 첨가제로 판단되었다.

LNG 수송선 적용을 목적으로 하는 PUF에 이러한 결과를 적용하였으며 대량 생산된 PUF를 이용하여 단열성능, 기계적 강도, 선팽창계수(CTE), 열충격 등을 측정하여 LNG carrier의 적용 가능성을 점검하였다. 평가 결과 제작된 경질 PUF의 열전도도를 사용하여 계산한 BOR은 0.12 %/day 이하로 최근 들어 강화된 BOR 사양을 충족시켜주는 것으

로 계산되었으며 기계적 강도 및 열적안정성 등도 LNG 수송선 사양을 충족시켰다.

결론적으로, 본 연구는 환경친화적 발포제로 제작한 폴리우레탄 폼을 단열재로 사용하고 낮은 BOR를 나타내는 LNG 수송선의 사용을 유도함으로서, 성층권의 오존층을 보호하고 소실되는 에너지를 줄여 환경보호에 기여할 것으로 기대된다. 또한, 차후 새로운 4세대 발포제를 사용하는 폴리우레탄 폼의 성능 개선을 도모하는 혼합시스템(blending system) 개발에 도움을 주고 이의 개발에 소요되는 시간을 줄여줄 수 있을 것으로 기대된다.

주요어: 폴리우레탄 폼, 단열재, 발포제, 오존 파괴 지수, 첨가제, 열전도도

학번: 2010-31014
성명: 이 영 범